Accepted Manuscript

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Key Multi(Ferrocenyl) Complexes in the Interplay between Electronic Coupling and Electrostatic Interaction

Saverio Santi, Annalisa Bisello, Roberta Cardena and Alessandro Donoli

In this review, the properties of the most significant examples of multi(ferrocenyl) cations containing a number of ferrocenyl units from two to six will be discussed and the results compared with the outcomes of some of our recent works on conjugated ferrocenyl complexes, trying to give an overview on how the electronic and electrostatic properties of the molecules.

Concomitantly, Cowan and co-workers focused their research on biferrocene and other bis(ferrocenyl) complexes, establishing the crucial role of the ferrocenyl moiety in the mixed-valence field. Bimetallic and multimetallic complexes are often precursors of mixed-valence species generated by chemical or electrochemical activation and several reviews have been devoted to this topic. The redox, optical and magnetic properties of these compounds depend on the extent of the metal–metal interaction among the metals.

In this Perspective article, the electronic and electrostatic properties of, to our opinion, the key multi(ferrocenyl) cations containing a number of ferrocenyl units from two to six will be discussed. Some of our recent works on conjugated ferrocenyl complexes will be considered and compared with the most significant examples reported in literature. We will try to give a comparative overview on how the nature of the bridging ligand, the distance among the redox-active centres, and the medium affect the electronic and electrostatic properties of the molecules.

Particular attention will be devoted to the bis(ferrocenyl) and tris(ferrocenyl) derivatives, showing as the latter should provide the means of bridging the gap between the interpretation of the related charge and electron transfer processes in simple bimetallic molecules and that in multicomponent systems.

A validation for this experimental evidence arises predominantly from the classification proposed by Robin and Day and the classical Marcus-Hush theory.

Theoretical aspects

According to Robin and Day, mixed-valence species are ordered into three classes, depending on the extent of charge transfer or delocalization. The strength of electronic interaction between the oxidized and reduced sites ranges from essentially zero (Class I) to
weakly or moderate (localized valence, Class II), to very strong electronic coupling (delocalized valence, Class III).

For a moderate coupled, class II, bimetallic system, the mixed-valence situation is described by the equilibrium between two ground states involving trapped-valence systems (Class II), in which a vectorial electron transfer from $M_1$ to $M_2$ occurs and vice versa (eq. 1):

$$M_1 \rightarrow M_2 \rightarrow M_1$$

The accessibility of the charge delocalized transition state (or excited state) allows the occurrence of the inter-valence charge transfer (IVCT), i.e. a metal-to-metal charge transfer (MMCT). In the case of a delocalized, class III, bimetallic system, there is no thermal barrier to electron transfer and the two metal ions hold formally averaged oxidation state in the ground state, that is 2.5 for a mono-oxidised bis-iron(II) complex. The actual situation is a resonance between two mesomeric structures (eq. 2):

$$M_1 \overset{\lambda}{\rightarrow} M_2 \overset{\lambda}{\rightarrow} M_1$$

Thus, the MMCT transition corresponds to an electron density distribution within the metal centred orbital(s) and the rate of the electron transfer is representable as electron mobility within this orbital(s). Intramolecular metal-to-metal electron transfer can be theoretically inspected using the classical model introduced by Marcus. According to Marcus, the potential energy surface of a degenerate mixed-valence system can be described by two parabolic curves, $G_a = \lambda q^2$ and $G_b = \lambda(1-q)^2$, which represent the non-interacting (diabatic) states as a function of a global reaction coordinate “$q$”. The electronic coupling of these two diabatic states corresponds to the electronic wavefunction mixing and produces two interacting (adiabatic) surfaces of energy $G_1$ (ground state) and $G_2$ (excited state), avoiding crossing in the intersection region. The schematic representation for a bimetallic complex is drawn in Fig. 1.  

Hush applied the Marcus theory to the issue of inter-valence transitions. The energy surface for thermal electron transfer is obtained from a two-state classical model in which the electronic interaction between diabatic surfaces is the off-diagonal matrix element $H$ in a 2x2 secular determinant. The solution gives eq. 3 which allows calculating the adiabatic energy surfaces represented in Fig. 1 in which the surface splitting at the avoided intersection results twice the value of electronic coupling $H$:  

$$G_1 = \frac{1}{2}[(G_a + G_b) - |(G_a - G_b)^2 - 4H^2|^{1/2}]$$

$$G_2 = \frac{1}{2}[(G_a + G_b) + |(G_a - G_b)^2 - 4H^2|^{1/2}]$$

For a weakly coupled Class II system, when the surface splitting is smaller than the reorganization energy ($2H << \lambda$), the vertical separation is almost equal to $\lambda$ (Fig. 1a). The electronic mixing $H$ causes the appearance of a double minimum adiabatic surface in the ground state with a maximum corresponding to the thermal electron transfer barrier $\Delta G^*$ given by eq. 4:  

$$\Delta G^* = \frac{\lambda^2}{4} - H + \frac{H^2}{\lambda}$$

Two electron transfer paths are viable: (i) the thermal process where the system moves from one minimum of the low lying adiabatic surface over the energy barrier $\Delta G^*$; (ii) the optical process where a vertical transition promotes the system from one minimum of the lower adiabatic surface to the upper adiabatic surface.

**Experimental techniques**

1. **Near infrared spectroscopy**

A powerful probe for evaluating the magnitude of the metal–metal interaction in mixed-valence compounds involves analysis of the inter-valence charge transfer (IVCT) absorption in near infrared (NIR) region. The maximum energy of this IVCT transition is $\nu_{max} = \lambda$ and is usually observed as a low energy and broad band in the NIR spectrum.

In the case of strongly coupled class III systems, the surface splitting is greater than the reorganization energy ($2H >> \lambda$), the resulting adiabatic ground-state surface displays a single minimum and $\Delta G^*$ disappears at $H = \lambda/2$, as predicted by eq. 4. The odd electron is now delocalized between the metal centres and $\nu_{max} = 2H$ (see Fig.1b).

For a class II system, Hush theory deduces the relationships associated to the characteristics of the IVCT band (eqs. 5–7). The energy of the inter-valence band is predicted to be dependent of $\Delta G^*$ (eq. 5):  

$$\nu_{max} = 4\Delta G^*$$

The magnitude of $H$ is related to the maximum energy $\nu_{max}$, the molar absorption coefficient $\varepsilon_{max}$, the half-bandwidth $\Delta\nu_{max}$ of the IVCT absorption, and the true electron transfer distance $r$:  

$$H = \frac{0.0206}{r} \sqrt{\nu_{max}\Delta\nu_{max}\varepsilon_{max}}$$
When the electronic coupling is pronounced, \( r \) can be considerably shorter than the geometric distance \( r_g \). The value of \( \Delta \tilde{v}_{\text{max}} \) for a localized mixed-valence system is predicted by eq. 7,

\[
\Delta \tilde{v}_{\text{Q2}} = \sqrt{16RT \ln 2 \tilde{v}_{\text{max}}} 
\]

(7)

that at the limit of high temperature (\( H \gg k_B T, T = 298 \text{ K} \)) gives eq. 8:

\[
\Delta \tilde{v}_{\text{Q2}} (\text{cm}^{-1}) = \sqrt{2310 \tilde{v}_{\text{max}}} 
\]

(8)

Two fundamental reviews on the application of Hush theory to mixed-valence complexes of transition metal centres are those by Creutz\(^{16}\) and by Crutchley\(^{17}\). Eqs. 7 and 8 are valid only for Gaussian-shaped bands and a rigorous quantum chemical formulation was given by Cave, Newton and Sutin\(^{18}\).

The assignment of a bimetallic mixed-valence system to class II or class III is usually based on the comparison between the experimental half-bandwidth and that calculated by means of eq. 7. If the values are similar, the valence state is considered class II; if the experimental half/bandwidth and that calculated by means of eq. 7, class III is usually based on the comparison between the observed and calculated half/bandwidths,

\[
\Delta \tilde{v}_{\text{Q2}} = \sqrt{16RT \ln 2 \tilde{v}_{\text{max}}}
\]

and that at the limit of high temperature (\( H \gg k_B T, T = 298 \text{ K} \)) gives eq. 8:

\[
\Delta \tilde{v}_{\text{Q2}} (\text{cm}^{-1}) = \sqrt{2310 \tilde{v}_{\text{max}}}
\]

According to Sutton and Taube\(^{21}\) for most of mixed-valence complexes the first four factors mainly contribute to the magnitude of \( \Delta G_c \). In eq. 11, \( \Delta G_c \) reflects the statistical distribution of the disproportionation reaction: in an electrochemical experiment with a molecule containing \( n \) noninteracting equivalent redox centres, one should observe a separation of \( \Delta E = \frac{n}{2} \Delta \tilde{v}_{\text{max}} \) (for \( n = 2 \) \( \Delta E = 36 \text{ mV} \), \( K_c = 4 \), \( \Delta G_c = 3.5 \text{ kJ} \) at 298 K),\(^{23} \) a rather smaller value than that measurable with the common electrochemical techniques. \( \Delta G_c \) represents the electrostatic repulsion between two charged metal centres, \( \Delta G_i \) is the inductive factor dealing with the competitive coordination of the bridging ligand by the metal ions, and \( \Delta G_p \) accounts for the free energy of resonance exchanges, the only contribution to \( \Delta G_c \) denoting real metal-metal coupling. Sutin and Crutchley\(^{20}\) pointed out early that another term, \( \Delta G_c \), must be considered if antiferromagnetic exchange significantly stabilizes the doubly oxidized reactant complex of eq. 10. However, in systems where superexchange occurs via the electron transfer pathway, the magnitude of \( \Delta G_c \) should be small or insignificant. Finally, Geiger has shown that ion pairing can have a strong effect on \( \Delta G_c \) and the ion-pairing factor \( \Delta G_p \) either increases or decreases its magnitude depending on the charge of the complexes in eq. 10. The magnitude of \( \Delta E \) has been frequently interpreted as a measure of the interaction between the metals. However, a cautionary warning on the use of the electrochemical data is required. In particular, the medium properties, i.e. the dielectric constant or the donor number of the solvent together with the nucelophylicity or ion-pairing ability of the supporting electrolyte can dramatically modify \( \Delta G_c \).

The importance of the electrostatic interaction was demonstrated by Sutton and Taube\(^{21}\): by evaluating the electronic contribution by mean of the Hush analysis, they established that the electrostatic effect explains most of the observed stabilization energy of the mixed-valence state. This means that electrochemical separations (\( \Delta E \)) may be observed in the absence of any electronic interactions. On the other hand, an undetectable or small \( \Delta E \) is not diagnostic of a negligible communication since, even in the case where a single electrochemical wave is observed, a significant amount of mixed-valence species may be present in solution.\(^{23} \)

The dependence of \( K_c \) on metal-metal distance was discussed by Hush.\(^{25} \) When the metal centres are separated by a large distance, \( K_c \) becomes smaller and more difficult to measure. It is possible to estimate \( K_c \) by using a simple theory considering that the deviation of \( K_c \) from the entropic factor of 4 is due to the electrostatic repulsion energy of the metal charges. Thus, a plot of \( \ln K_c \) vs \( 1/r_g \) (\( r_g \) is the geometric distance) should be linear and pass through \( K_c = 4 \) for \( 1/r_g \to 0 \).

The only factor of \( \Delta G_c \) which accounts for “real” metal-metal coupling is \( \Delta G_c \). We can break\(^{25} \) \( \Delta G_c \) into two contributions (eq. 12),
\[ \Delta G_r \approx \Delta G_{nr} + \Delta G_r \]

In the case of a symmetrical weakly coupled II complex, it has been shown \(^{27}\) that the resonance stabilization is given by eq. (13):

\[ \Delta G_r = 2H^2 \lambda - 2H^2 \nu_{\max} \]

For a class III complex, \(\Delta G_r\) is predicted by eq. (14):

\[ \Delta G_r = 2(H - \lambda/4) = \nu_{\max} - \lambda/2 \]

It obviously results that \(\Delta G_r = \nu_{\max} / 2\) for a borderline system \((H = \lambda)\) and \(\Delta G_r \rightarrow \nu_{\max}\) for very strongly coupled systems \((H >> \lambda)\).

**Bis(ferrocenyl) complexes**

The series of bis(ferrocenyl) polyenes of general formula Fe(CH=CH)\(_n\)Fe (1a–e, \(n = 1–6\)), prepared by Launay and Spangler,\(^{27}\) offered a unique opportunity to study accurately the IVCT transition and the decay law of the electronic interaction with distance.

![Diagram of bis(ferrocenyl) polyenes](image)

The study of the mixed-valence species obtained by monoxidation of 1a–e showed that the IVCT transition appeared at markedly low energy, and metal–metal electronic coupling existed even when the \(\Delta E\)splitting was not observed \((n = 4–6)\).

As expected, a plot of \(\ln K_c\) vs \(1/r_g\) was found linear and passed through \(K_c = 4\) for \(1/r_g = 0\) (Fig. 2a). The electrostatic interaction between the metal charges is the major effect in these compounds where the metal centres are separated by a large distance (7–18 Å). Describing the intermetallic coupling by using the two-state model, if this coupling is small as it must be in order that this model is appropriate,\(^{18}\) the Hush model allows \(H\) to be calculated from the parameters of the deconvoluted IVCT band (eq. 6).

From McConnell’s theory,\(^{28}\) the coupling should decrease exponentially as \(n\) increases according to eq. (15):

\[ H_e = H_0 e^{-\gamma n} \]

where \(\gamma\) is defined as a measure of the coupling drop. As far as the decay of the metal-metal coupling with distance along the series 1a–e, the plot of \(\ln H\) was found almost linear indicating that \(H\) decays exponentially with distance (Fig. 2b). The slope is 0.087 Å\(^{-1}\), corresponding to a decrease of a factor 2 for each 8 Å.

In order to circumvent isomerization problems, the complexes 2a and 3a and the related 1,2-diferrocenyl-cycloexene (4) were prepared by Kwan. The stability of their mixed-valence derivatives and of 4 was discussed mainly in terms of resonance delocalization and electrostatic repulsion energy. According to Hush analysis, the energy contribution due to the electrostatic repulsion dominates the overall stability of the mixed-valence state in 2a, 3a*, and 4*, while the resonance delocalization contributes less than 4%.

The ortho (5o), meta (5m) and para (5p) isomers of bis(ferrocenyl)benzene were prepared by Launay and Joachim.\(^{29}\) An experimental and theoretical study of the effect of topology on intervalence electron transfer was accomplished. Except for 5m, for which a single oxidation wave appeared whatever the electrochemical technique was used, the beginning of splitting was observed for 5o and 5p. Adapting a literature procedure,\(^{2b}\) \(\Delta E\) and \(K_c\) values were determined simulating the profiles of DPV measurements. Among the energetic factors which contribute to \(K_c\) values, the electrostatic interaction, strongly related to the distance between the redox centres, was assumed to be predominant.
Indeed, the ortho isomer 5o showed the highest $K_c$ value but the meta isomer 5m, having the intermediate iron–iron distance, provided the smallest $K_c$ value, indicating that the electrostatic interaction is not sufficient to explain $K_c$ variations. Despite the small $\Delta E$ splitting for 5o$^+$ (131 mV), 5p$^+$ (104 mV) and 5m$^+$ (90 cm$^{-1}$), intervalence transitions for these compounds were detected and the values of metal–metal couplings $H$, calculated from the intervalence band parameter using Hush’s relationship (eq. 6), resulted in the order $5p^+$ (347 cm$^{-1}$) > $5o^+$ (202 cm$^{-1}$) > $5m^+$ (161 cm$^{-1}$). The fading of the interaction in 5m$^+$ was attributed to a quantum interference effect, i.e., a cancellation of the contributions of the two-electron transfer paths.

An electrochemical study on a series of ortho- (6o), meta- (6m) and para- (6p) bis(ferrocenyl)ethynylbenzenes was carried out by Astruc$^{20}$ in order to get insight into the electrostatic or resonant nature of the interaction between ferroceny groups.

Previously, 1-bromo-3,5-bis(ferrocenylethynyl)benzene was reported by the Long and Zanello$^{31}$, for which only one oxidation wave was observed by CV accounting for a lack of electronic communication between the redox centres. Other poly(ferrocenyl) complexes resulted in the observation of a single wave in CV using $nBu_4NPF_6$ as the supporting electrolyte.$^{32}$

Weakly coordinating anions with highly delocalized negative charge, such as $\text{B(C_2F}_5\text{)}_4$ and $\text{BARF}_2$, as supporting electrolyte [$\text{BARF}_2 = 3,5$-bis(trifluoromethyl)phenyl], allow minimization of nucleophilic attack on the radical cations. In addition, they undergo much weaker ion pairing than the traditional anions in low-polarity solvents. These properties make it possible to manipulate the anodic $\Delta E$ values, and the largest values are obtained in less polar solvents with low donor number.$^{23a}$

CVs of 6m of 6p showed a single two-electron wave with $nBu_4NPF_6$ or $nBu_4NBARF_2$ as the supporting electrolyte, a result attributed to the absence of both electronic and electrostatic interaction. The ortho isomers 6o showed a single two-electron wave using $nBu_4NPF_6$ due to the lack of significant electronic communication between the two ferrocenyl redox centres. However, wave splitting is observed for 6o with $nBu_4NBARF_2$, which was ascribed to the presence of significant electrostatic repulsion between the two “naked” cationic centres in 6o$^{2+}$.

There is evidence that traditional anions such as $\text{BF}_4^-$ and $\text{PF}_6^-$ may react as nucleophiles with radical cations.$^{20}$ Astruc suggested that the $\Delta E$ corresponds approximately to the electronic communication in the absence of other significant factors if a splitting between two CV waves of two equivalent redox centres is observed.$^{30}$ However, it must keep in mind that an undetectable or small $\Delta E$ is not diagnostic of a negligible communication, even in the case where a single electrochemical wave is observed a significant amount of mixed-valence species may be present in solution.$^{31}$ The values of $K_c$ and $\Delta E$ determined by electrochemical measurements have been widely used for assessing the degree of electronic coupling in mixed-valence complexes. However, the electronic-coupling parameters derived from classical and semiclassical theoretical models$^{13a,b,15b,26}$ and from electrochemical studies are frequently in poor agreement.$^{23}$ Caution is needed in the interpretation of electrochemical data due to the considerable dependence of redox potential and reversibility on the nature of the solvent and supporting electrolyte.

Much better results and agreement with the theoretical treatment are usually provided by optical investigations in the NIR region where mixed-valence species typically absorb.

Indeed, we have recently synthesized the bis(ferrocenyl) complexes of s- and as-indacenes, 7a and 7b, demonstrating that the rigid and planar indacene platform bonded to two terminal redox groups displays a redox chemistry that can be switched from a single two-electron transfer, using $nBu_4NPF_6$ as the supporting electrolyte, to two successive one-electron transfers with $nBu_4NB(C_2F_5)_4$.

Despite the small $\Delta E$ values even in the presence of $nBu_4NB(C_2F_5)_4$, resolved by square wave voltammetry (Fig. 3), generation by chemical oxidation of the mixed-valence diiron catons and their characterization by optical spectroscoopy were accomlished. Hush analysis of the IVCT bands in the NIR region indicated that 7a$^\text{II}$ and 7b$^\text{II}$ are Class II, moderate coupled, mixed-valence systems.

---

**Fig. 3.** Oxidative CVs in dichloromethane at 20 °C of 7a with (a) 0.1 M $nBu_4NPF_6$, (b) 0.1 M $nBu_4NB(C_2F_5)_4$, (c) DPV with 0.1 M $nBu_4NB(C_2F_5)_4$. Oxidative CVs in dichloromethane of 7b with (d) 0.1 M $nBu_4NPF_6$, (e) 0.1 M $nBu_4NB(C_2F_5)_4$, (f) DPV with 0.1 M $nBu_4NB(C_2F_5)_4$. Reprinted with permission from *Organometallics*, 2011, 30, 1116. Copyright 2011 American Chemical Society.
Moreover, \( \Delta E \) separation was sensitive to the geometry of the organic bridge. In particular, as a result of higher \( \Delta E \) separation, 7b\(^+\) could be selectively produced in solution. The molar absorption coefficient of its IVCT band was higher than that of 7a\(^+\), suggesting that the linear “para-like” s-indacene is a more efficient bridging ligand than the non-linear \( \alpha,\alpha\)-s-indacene in transmitting charge from the ferrocene to the ferrocenium terminal groups.

Similarly, as previously reported by Coudret and Launay,\(^{35} \) a single wave was observed for the bis(ferrocenyl)anthracene complex 8 and its TCNE adduct 9 at the same potential, corresponding to two close mono-electronic processes.

\[
\begin{align*}
8 & & 9
\end{align*}
\]

DPV allowed the resolution of the two processes and the determination of the \( \Delta E \) and \( K_d \) values for 8 (72 mV and 17, respectively). The mixed-valence cations 8\(^+\) and 9\(^+\) were generated by controlled potential electrolysis and the obtained spectra in the NIR region showed inter-valence transitions as broad bands. The resulting values of the electronic coupling parameters \( H \) were 260 cm\(^{-1}\) for 8\(^+\) and 150 cm\(^{-1}\) for 9\(^+\), indicating significant electronic interaction for both the mixed-valence species. Interestingly, in the latter, \( H \) decreases but does not vanish despite the loss of conjugated character.

In its early works,\(^{36} \) Rausch described the synthesis of a series of compounds where up to four ferrocenyl groups are introduced on the cyclobutadiene ring of \( \eta^2\)-cyclobutadiene(\( \eta^5\)-cyclopentadienyl)Co, among which the two bis(ferroceny1) isomers cis-CpCo(FcPh\(_2\)C\(_6\)H\(_4\)) (10a) and trans-CpCo(Fc\(_2\)Ph\(_2\)C\(_6\)H\(_4\)) (10b) were examined with the aim to inspect the effect of positional isomerism on the properties of the mixed-valence species 10a\(^+\) and 10b\(^+\).

\[
\begin{align*}
10a & & 10b
\end{align*}
\]

Within CV experiments in dichloromethane containing \( nBu_4NPF_6 \) as the supporting electrolyte, both ferrocenyl groups of 10a and 10b isomers underwent two successive reversible oxidations at almost identical potentials separated by 190 and 170 mV, respectively.

Surprisingly, both mono and dioximated forms of the two isomers gave rise to a band in the NIR region (10a\(^+\), \( \tilde{\nu}_{\text{max}} = 8000 \text{ cm}^{-1} \); 10b\(^+\), 8930; 10b\(^\text{ii}+\), 6950; 10b\(^\text{ii}+\), 9260) characterized by position, intensity, bandwidth, and solvent dependence typical of IVCT bands of class II mixed-valence species. Since an iron–iron coupling is not possible in the dications, the authors proposed that the inter-valence transition arose predominantly from a Co(I)–Fe(III) coupling. This hypothesis was corroborated by the observation that the cation of the monoferrocenyl CpCo(Fc\(_2\)Ph\(_2\)C\(_6\)H\(_4\)) exhibited a band in NIR region (\( \tilde{\nu}_{\text{max}} = 7840 \text{ cm}^{-1} \)) similar to those seen for 10a\(^{\text{ii}+}\) and 10b\(^{\text{ii}+}\).

Burrell and Officier\(^{37} \) reported synthesis, structure and properties of bis(ferrocenyl)porphyrins, the \( \alpha,\alpha\)-5,15-bis(ferrocenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin 11 and its nickel derivative Ni-11, for which a strong coupling between the two remote ferrocenyl moieties resulted upon single electron oxidation.

The CV of 11 and Ni-11 showed two successive ferrocene-based oxidation waves separated by 190 and 410 mV, respectively. The large values of \( K_d \) calculated from the separation of the voltammetric waves, \( 1.6 \times 10^5 \) for 11 and \( 8.5 \times 10^4 \) for Ni-11, were consistent with the appearance, upon one electron oxidation, of low energy IVCT absorptions (at 1080 and 946 nm, respectively). The comparison of the small bandwidth \( \Delta \tilde{\nu}_{\text{21}} = 1400 \text{ cm}^{-1} \) for Ni-11\(^+\) with the value calculated by mean of eq. 8 (4900 cm\(^{-1}\)) indicates that this cation is a class III (highly delocalized) mixed-valence species. For 11\(^+\), the experimental value \( \Delta \tilde{\nu}_{\text{21}} = 2600 \text{ cm}^{-1} \), compared to the calculated value (4600 cm\(^{-1}\)), suggests a borderline class II/III behaviour. Accordingly to the trend of the electrochemical \( \Delta E \) splitting, the nickel coordination strongly enhanced the magnitude of the iron–iron coupling. Similar effect was found by the metal-free and nickel-coordinated RR-5,15-bis(ferrocenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetraethylporphyrin.\(^{38} \)

The metal–metal interaction in both 11 and Ni-11, at a separation more than 10 Å, is remarkably high and quite unexpected if considering that the related 5,10,15,20-tetraferrocenylporphyrin and 5,15-diferrocenyl-10,20-di-p-tolylporphyrin\(^{39} \) display no such coupling.

A DFT calculation suggested that this strong coupling should be the result of extensive mixing of both ferrocenyl molecular orbital systems with that of the porphyrinic \( \pi \)-system. The low symmetry (\( = C_2 \)) of 11 and Ni-11, the possibility of extensive vibronic coupling owed to the restricted rotational flexibility of the ferrocenyl groups and transmitted into the porphyrin core, and the molecular dipole created by the \( \alpha,\alpha \)-porphyrin are the possible factors that may rationalize the strong coupling.

In order to understand how the ferrocenyl substituents located at specific \( \text{meso} \) positions in bis(ferrocenyl)porphyrins can influence long-range metal-metal coupling, two structural isomers of meso-substituted (bis)ferrocenyl-dipentafluorophenyl porphyrins, the “trans” with the ferrocenyl groups in the 5,15 positions, 12, and the “cis” with the ferrocenyl groups in the 5,10 positions, 13, were prepared and characterized by Swart.\(^{40} \)

While CV experiment of 12 in the coordinating acetonitrile, using the traditional \( nBu_4NPF_6 \) supporting electrolyte, resulted in the overlapping of two oxidation waves, the CV and SWV experiments, conducted in dichloromethane in the presence of the low ion-pairing \( nBu_4NB(C_6F_5)_4 \) as supporting electrolyte, displayed two resolved waves but no significant differences between the first and second ferrocene-centred oxidations of two isomer isomers (111 mV for 12 and 115 mV for 13) were found.
The observed splitting with $n$Bu$_2$NB(C$_6$F$_5$)$_4$ was mainly attributed to the presence of significant electrostatic repulsion between the two nonion-pairing cationic centres in the dication. However, since the optical properties of the 12$^+$ and 13$^+$ were not reported, the nature of the electronic coupling of these cations was not clarified.

In this context, addressing the question if the $r$ system of the porphyrin is an efficient platform for electron transfer between ferrocenyl moieties, Nemykin and Galloni$^{41}$ prepared and characterized the “$trans$” 5,15-bis(ferrocenyl)-10,20-diphenyl (14) and the “$cis$” 5,10-bis(ferrocenyl)-15,20-diphenyl (15) porphyrins.

The electrochemical removal of individual electrons from the ferrocene substituents indicated the existence of long-distance metal-metal interaction in both the $cis$ and $trans$ isomers, a result supported by spectroelectrochemical and chemical oxidation experiments. Within CV experiments, the first oxidation of $trans$ 14 occurred at lower potential than that of $cis$ 15 and the $\Delta E$ separation between the two ferrocenyl-based oxidation waves of 14 and 15 were 208 mV and 150 mV, respectively. The related comproportionation constants are large enough to form stable mixed-valence species.

The analysis of the IVCT bands observed in the NIR region found for the mixed-valence cations 14$^+$ and 15$^+$ ($\tilde{\nu}_{max}$ = 11700, 11000 cm$^{-1}$, $\tilde{\nu}_{max}$ = 9300, 6100 M$^{-1}$ cm$^{-1}$ and $\Delta\tilde{\nu}_{1/2}$ = 2900, 4100 cm$^{-1}$, respectively) and formed under spectroelectrochemical and chemical oxidation conditions, suggested the existence of electron localization and class II behaviour in the Robin-Day classification.

The values of the parameter $H$ determined for 14$^+$ and 15$^+$ (910 and 1100 cm$^{-1}$, respectively) using the DFT calculated iron–iron distances as $r$ in eq. 6, suggested somewhat higher metal electronic coupling in the $cis$ isomer. However, when the electronic coupling is pronounced, the true electron transfer distance $r$ can be considerably shorter than the geometric distance $r_g$. Indeed, we note that the narrowness of the bands highlighted by comparing the experimental and calculated (eq. 8) half-bandwidths $\Delta\tilde{\nu}_{1/2}$ was more pronounced for the $trans$ 14$^+$. The value of the parameter $f$ (eq. 9) found for 14$^+$ (0.44) results higher than that of 15$^+$ (0.19) clearly suggesting, to our opinion, that the $trans$ disposition of the ferrocenyl groups significantly increases the strength of the metal–metal interaction with respect to that of the $cis$ configuration. In addition, the observation that the molar absorption coefficient of the IVCT band of 14$^+$ is higher than that of 15$^+$ supports the proposition that the $trans$-substituted porphyrin is a more efficient bridging ligand than the $cis$ in transferring the electron from the ferrocene to the ferrocenium groups. This conclusion was confirmed by Bucher for the $cis$ 5,10-bis[1’-[2-(1,3-dithiolanyl)]ferrocenyl]-15,20-di(p-tolyl)porphyrin and $trans$ 5,15-bis[1’-[2-(1,3-dithiolanyl)]ferrocenyl]-10,20-bi(p-tolyl)porphyrin,$^{32}$ although based only on the value of the voltammetric $\Delta E$ splitting.

In a series of papers$^{43}$ recently reviewed by the same author,$^{44}$ Lang described an elegant method allowing the calculation of the effective electron transfer distance within a specific series of molecules and of the different contributions to $\Delta G_c$ ($= -F\Delta E$) given by the statistical distribution ($RT/F$)$\ln(1/4)$, the electrostatic interaction ($\Delta G_e$), the inductive factor ($\Delta G_i$), and the resonance stabilization ($\Delta G_r$). To this purpose, a family of bis(ferrocenyl) five-membered heterocycles (16–24) was prepared and analysed.

Electrochemical CV and SWV measurements were carried out in dichloromethane in the presence of $n$Bu$_2$NBPF$_6$ or $n$Bu$_2$NB(C$_6$F$_5$)$_4$ as the supporting electrolyte. The use of dichloromethane and $n$Bu$_2$NB(C$_6$F$_5$)$_4$ resulted in a better resolution due to the lower ion-pairing capabilities of B(C$_6$F$_5$)$_4$. Besides the higher quality of the electrochemical data for multiredox processes, the increase of wave splitting observed using the fluorinated electrolyte mostly reflects the electrostatic contribution to the stability of mixed-valence monocationic molecules. The enlargement of the wave separation is similar along the series 16–19 (130–140 mV),$^{32a,34c,35}$ Therefore, taking into account that the iron–iron distances in this series are almost equal, electrostatic interactions should result similar.

A comparison with analogous bis(ferrocenes) featuring 1H-phospholes bridges revealed similar trends of the electrochemical properties, with the result that the more easily oxidized complexes bearing the more electron donating heteroatoms gave rise to larger $\Delta E$ values and accordingly higher stability of the corresponding mixed-valence cations, in the sequence NPh (450 mV) > NMe (410 mV) > O (290 mV) ≈ PPh (280 mV) > S (260 mV).

It was found that the more electron rich the heterocyclic bridge was, the higher $\Delta E$ splitting appeared, an effect attributed to changes in the electron transfer properties of the connecting heterocycle. Assuming that the distances between the two ferrocenyl sites are similar along the series 16–24, all the factors contributing to $\Delta G_c$ are constant with exception of the resonance stabilization $\Delta G_r$:

$$\text{const} = RT\ln(1/4) + \Delta G_e + \Delta G_i$$

(16)

For the cations 16$^+$–24$^+$, the oscillator strength $f^{15a,17}$ of the IVCT absorptions increases with the degree of intermetallic communication:

$$f = (4.6\times10^{-3})\nu_{max}^{1/2}$$

(17)

The cations 16$^+$–24$^+$ showed a linear relationship between $\Delta E$ and $f$ as predicted by eq. 16 for a series of molecules with similar geometries and electrostatic properties. This relation could be described for the first time in organometallic chemistry and offers the possibility to estimate $r$ which is difficult to obtain experimentally. In fact, combination of eqs. 16 and 17 lead to a linear relationship between the oscillator strength $f$ and $\Delta E$ (Fig. 4).
From the slope, the effective electron transfer distance $r$ was calculated ($2.05 \pm 0.05$ Å), much shorter than the geometrical iron–iron distances, and used to determine $H$ parameters according to Hush equation (eq. 6).

$$
\frac{f}{4.6 \times 10^{-9}} = \frac{\text{const} \times r^2 + F \times r^2}{8.49 \times 10^{-4}} \Delta E
$$

(18)

Finally, from the intercept and by using eqs. 13 and 16, the contributions to $\Delta G_e$ were calculated as the sum of the electrostatic and inductive factors ($\Delta G_e = \Delta G_i + \Delta G_r$) and of the resonance stabilization ($\Delta G_r$).

Barlow and O’Hare$^{47}$ synthesized a series of mixed bis(ferrocenyl) complexes in which two FeCp*Cp (Cp* = pentamethylcyclopentadienyl) are linked by the saturated bridges CMe$_2$, SiMe$_2$, GeMe$_2$, and Si$_2$Me$_4$. SWV of 25–27 showed that the $\Delta E$ separation between the oxidation waves decreases for the bridging group X in the order CMe$_2$ > SiMe$_2$ > GeMe$_2$, a result consistent with the increasing metal–metal distance with a through-space and essentially electrostatic effect which likely dominated the value of the related comproportionation constant $K_c$.

The electronic coupling was quantitatively probed by the analysis of the IVCT absorption of mixed-valence cation in the NIR region. The electronic coupling parameter $H$ was determined by analysis of the IVCT band using Hush’s relationship (eq. 6) and the cation 25$^+$–27$^+$ were classified as Class II mixed-valence species. In a Class II system, the $\tilde{\nu}_m$ energy of the IVCT band represents the reorganisation energy $\lambda$ for the intramolecular electron-transfer reaction. The value of $\tilde{\nu}_m$ slightly increases with the size of the bridging atom, likely due to differences in external reorganisation energy: as the metal–metal separation increases, the electron transfer distance will increase and consequently the solvent reorganisation parameter becomes larger.

The degree of electronic coupling decreases in the order CMe$_2$ > SiMe$_2$ > GeMe$_2$. This observation is unusual if compared with previous results on metalloccenes linked by saturated bridges. In those studies, a stronger coupling through a Si-bridge was suggested, due to conjugation through empty, low-lying $\sigma^*$ or $d$ orbitals of Si, which may enable greater coupling.$^{39}$

Differently, Barlow and O’Hare suggested that the decrease in the order CMe$_2$ > SiMe$_2$ > GeMe$_2$ indicates that the coupling in 25$^+$–27$^+$ is predominantly through space. Assuming the same molecular conformation, the metal–metal separation should increase with the size of the bridging atom; hence, the distance parameter $r$ in eq. 6 should increase and the value of $H$ calculated for the SiMe$_2$ and GeMe$_2$ systems may be overestimated, reinforcing the observed trend. Moreover, the observation of a strong IVCT band for 28$^+$ pointed out the importance of a strong through-space coupling.

We have recently reported the synthesis of a new series of 3$_{10}$-helical peptides of different length (29–33) based on the strongly foldameric $\alpha$-aminoisobutyric (Aib) and containing two terminal ferrocenyl units.\cite{29}

\begin{align*}
25, X &= \text{CMe}_2 \\
26, X &= \text{SiMe}_2 \\
27, X &= \text{GeMe}_2 \\
28, X &= \text{Si}_2\text{Me}_4
\end{align*}

The intrinsic redox asymmetry of the C-terminal and N-terminal ferrocenyl groups permitted to generate, selectively, the cationic and dicationic derivatives. The end-to-end effects of the charge holes generated by single and double oxidations were analysed by means of electrochemical and spectroelectrochemical techniques. The results indicated that charge transfer across the peptide occurs in the five peptides. In particular, in the pentapeptide (33), charge is transferred through an intramolecular iron–iron separation of 14 Å. The trends of the oxidation potentials, previously observed by us in the two series of monometalllic ferrocenyl-peptides,\cite{34} depend on the position of the ferrocenyl groups in the chain and on the macrodipole orientation (Fig. 5).

Indeed, as the (Aib)$_n$ peptide grows, oxidation of the ferrocenyl occurs easier or harder depending on the orientation of the macrodipole moment of the peptide chain, that is away from the N-terminal Fe or towards the C-terminal ferrocenyl moiety, respectively. Since no IVCT band was observed, these effects can be ascribed to inductive and/or electrostatic interaction transmitted through the intramolecularly hydrogen-bonded networks.

The strongest effect is observed for tripeptide 31 in which two intramolecular C=O···H–N hydrogen bonds are formed, establishing a particularly efficient electron transfer shortcut.\cite{35}
Metal–metal electron delocalization in linkage structures assembled via noncovalent are extremely rare. Kaimfer16 reported the preparation and properties of a ferrocene derivative containing a quadruple hydrogen bonding motif designed to self-recognize, forming a fascinating highly stable hydrogen-bonded dimer that contains two identical ferrocene centers separated by more than 10 Å (34).

CV experiments with 34 in acetonitrile/nBu4NPF6 solution showed one reversible oxidation waves at 0.43 V vs Ag/AgCl, but enriching the solvent mixture in dichloromethane, a solvent less polar than acetonitrile, a second reversible oxidation waves at 0.82 V vs Ag/AgCl appeared. The stability of the mixed-valence dimer 34+ in dichloromethane solution allowed the detection of an ICT band in the NIR spectral region at $\nu_{\text{max}} = 8370 \text{ cm}^{-1}$. Surprisingly, the spectral characteristics, in particular the experimental bandwidth ($\Delta \nu_{1/2} = 560 \text{ cm}^{-1}$) compared to the value predicted by Hush theory (eq. 6, $\Delta \nu_{1/2} = 4400 \text{ cm}^{-1}$), indicated that the extent of electronic coupling between the ferrocenyl moieties in the dimer is extremely strong and 34+ is a totally delocalized class III system with very high $\Gamma$ parameter (0.87) in the Robin-Day and Brunschwig-Creutz-Sutin classifications. Remarkably, this is the first example, and to the best of our knowledge unique so far, of a noncovalent mixed-valence species, constituted by two identical halves assembled by four hydrogen bonds.

Applications in useful devices of compounds containing two or more connected ferrocenyl moieties are often problematic mainly because electronic coupling between the two redox sites rapidly decreases with metal–metal distance. A combination of factors influences the communication between the connected ferrocenes, including the type of connection, the length of the connector and the orientation of the two ferrocenes.

Among the molecules which are excellent benchmarks for testing the paradigm of quantum cellular automata (QCA), which is based on field-coupled charge containers, a symmetric mixed-valence complex is the simplest building block for a QCA cell. The binary states (the Boolean states) are obtained by changing the position of an electron from one metal centre to the other. Bis(ferrocenyl) mixed-valence complexes join the family of molecular electronics in the QCA paradigm and found a successful application with 3,6-bis(1-ethylferrocenyl)-9H-carbazol-9-yl-6-hexan-1-thiol (35) and its enantiomers.

In a QCA, the interplay between electronic coupling and electrostatic interaction is a crucial point; quantum dots are arranged in functional cells connected by tunnelling pathways, each containing two mobile charges which tend to localize on opposite corners due to electrostatic repulsion, encoding the Boolean states 1 and 0 (fig. 6).

The adjacent cells interact electrostatically and their ground state configuration depends on the reciprocal charge positioning in the cells. In fig. 6, the cell includes also two middle dots corresponding to a different ground state, imposed by an external electric field (the clock) which allows directional information flow.

Complex 35 addressed all the three requisites which are functionally demanded by QCA operation: (i) defined Boolean states were granted and readable, as the weak conjugation found between ferrocenyl groups favoured neat charge localization, keeping the Boolean states well distinct; (ii) the geometry of dots, which strongly affects electrostatic interaction, was stable after solid state immobilization; (iii) applying a proper clocking electric field could delete the previously stored state.

At room temperature and low scan rate (1 V s$^{-1}$), the CV of 35 in THF and nBu4NPF6 as the supporting electrolyte displayed one reversible two-electron oxidation peak at $E_{1/2} = 0.35 \text{ V}$ associated with the reversible oxidation of the two equivalent ferrocenyl moieties. However, the two-electron peak is split into two reversible one-electron peaks at high scan rate (10 V s$^{-1}$). The same effect was obtained at low temperature (218 K) and lower scan rate (1 V s$^{-1}$). At more positive potentials 35 underwent a further reversible
oxidation process with $E_{1/2} = 1.25$ V associated with the reversible oxidation of the carbazole unit.

These results indicated the existence of weak through-bond interaction between the ferrocenyl units allowing a description of 35° in terms of the localized redox sites. The observed weak conjugation favours neat charge localization keeping the Boolean states well distinct. Moreover, solid-state electrochemistry of mixed self-assembled monolayers (SAMs) of 35 and hexane-1,6-dithiols demonstrated the effective immobilization and stability of 35 on the surface and excluded undesired structural rearrangements upon application of the electric field. Finally, functionality simulation showed that charge localization on the carbazole can be obtained by clocking field values in the order of a few V nm⁻¹, so encoding a neutral state as required for a correct QCA operation.

Tris(ferrocenyl) complexes

Investigations on three families of tris(ferrocenyl) systems, namely “star-shaped”, linear and cyclic, should provide a mean of bridging the gap between the interpretation of the electron/transfer process in “star/shaped”, linear and cyclic, should provide a mean of bridging the gap between the interpretation of the electron/transfer process in

Homoleptic tris(ferrocenyl) “star-shaped” derivatives of B, N, P, Sb, Bi have been prepared and characterized so far (36-40). In addition, tris(ferrocenyl) compounds of PO (41), C (42) and Si (43) were also synthesized.

The charge transfer properties of a limited number of these molecules were investigated and those exhibiting electron transfer transition include the mixed-valence cations of tris(ferrocenyl)phosphine oxide (41) and tris(ferrocenyl)methane (42). For 42, the electronic coupling $H = 205$ cm⁻¹, estimated using the Hush relationship (eq. 6), is consistent with a mixed weakly coupled class II system.

Monoxided...
differ with respect to the nature and strength of the electronic interactions.

The CV of “star-shaped” 1,3,5-tris(ferrocenyl)ethynylbenzene complex 47 reported by Astruc30 showed a simultaneous oxidation of the three ferrocenyl substituents with nBu4NPF6 as the supporting electrolyte, attributed to the absence of electronic communication, and three well-separated redox events with nBu4BAR4N.

However, for meta-bis(ferrocenyl)ethynylbenzene (6m) as well as for the 1,3-bis(ferrocenylethynyl)arene complexes containing bromide (48), ethynyl (49), trimethylsilylthynyl (50) and pentamethyldiferrocenylethynyl (51) substituents in the third meta position, only a single wave was observed for the two ferrocenyl group even with nBu4NB(C6F5)4.

In these compounds, in order to minimize the electrostatic repulsion, the two oxidized ferrocenyl groups were supposed to lie at opposite sides with respect to the plane of the benzene ring. When a third ferrocenyl group is present in meta position, there is “frustration”, meaning that the third ferrocenyl must adopt an intermediate position enhancing the electrostatic effect among the three positively charged sites and causing the splitting of the three ferrocenyl CV waves.

As a result of the ΔE splitting, 53+ and 54+ can be selectively produced in solution.

“Frustration” in 47+ and 51+ R = H, Me

In the case of 51, the charge of pentamethylated ferrocenyl is partially shielded causing the decrease of the electrostatic interaction with the two other oxidized ferrocenyl that arrange at opposite sides in order to minimize their mutual repulsion.

We have recently described the synthesis, electrochemistry of a family of mono- (52), bis- (53) and tris(ferrocenyl) (54) complexes 47 of dihydro-1H-trindene (TdH),46 a polycyclic hydrocarbon synthesized by Katz and Ślusarek in the early 1980s.47 The use of TdH as a metal bridging ligand is particularly favourable because strain is minimal as a consequence of the presence of only five- and six-membered rings.

Complex 54 is a “star-shaped” tris(ferrocenyl) system structurally related to the diferrocenyl complex 7a previously investigated by us. Within CV and SQV experiments (Fig. 7), the bimetallic 53 and trimetallic 54 complexes display a redox chemistry that could be switched from a single to two consecutive oxidation processes by changing the supporting electrolyte from nBu4NPF6 to nBu4NB(C6F5)4.

By simple variation of the counter-ion of the supporting electrolyte PF6 with the weak nucleophilic and ion/pairing B(C6F5)4 anion, the unresolved two-electron oxidation wave of 53 is split into two consecutive one-electron oxidation waves. Similarly, the three-electron oxidation waves of 54 are partially resolved in two consecutive one-electron and two near simultaneously occurring one-electron oxidations oxidation waves.

Fig. 7 Oxidative CVs in dichloromethane, scan rate ν = 0.5 V s−1, of 53 with (a) 0.1 M nBu4NPF6, (b) 0.1 M nBu4NB(C6F5)4, (c) SWV with 0.1 M nBu4NB(C6F5)4. Oxidative CVs in dichloromethane of 54 with (d) 0.1 M nBu4NPF6, (e) 0.1 M [nBu4NB(C6F5)4], (f) SWV with 0.1 M nBu4NB(C6F5)4. Reprinted with permission from Organometallics, 2013, 32, 1029. Copyright 2013 American Chemical Society.

Hush analysis of the IVCT bands in the NIR region clearly indicated that 53 and 54 are class II mixed-valence systems. The narrowness of these bands was highlighted by comparing of the experimental and calculated half-bandwidths. Remarkably, the value of I found for the trimetallic 54 species is higher than that of bimetallic 53, which clearly suggests that the presence of the third ferrocenyl group in 54 significantly increases the strength of the metal–metal
interaction with respect to that of the structurally related diferrocenyl cation $53^-$. Significantly, as found for 7, 8 and 44, the absence of $\Delta E$ splitting with ion-pairing or nucleophylic supporting electrolytes was not indicative of lack of electronic coupling.

Pertaining to linear multi(ferrocenyl) systems, in one of its early works Meyer$^{66}$ reported the oxidation state and electron-transfer properties of linked 1,1'-triferrocene (55), 1,1',-tetraferrocene (56) compared with those of the parent biferrocene.

The CV displayed a number of reversible waves equal to the number of ferrocenyl groups in the oligomer complex. The pattern of the oxidation potentials accounted for the electron-donating properties of the ferrocenyl group, in the order biferrocene compared with those of the parent biferrocene.

Weakly electronic coupling was measured between Fe(II) and Fe(III) sites for the mixed-valence ions of 55$^+$. 55$^{52^-}$ and 56$^{57}$. In particular, the IVCT energy of the mixed-valence cation 55$^+$ detected in the NIR region ($\nu_{\text{max}} = 5590 \text{ cm}^{-1}$, $\epsilon_{\text{max}} = 1720 \text{ M}^{-1}\text{ cm}^{-1}$) was similar to that found for (Fc–Fe$^+$) ($\nu_{\text{max}} = 5260 \text{ cm}^{-1}$, $\epsilon_{\text{max}} = 760 \text{ M}^{-1}\text{ cm}^{-1}$), supporting valence localization (Class II) for the trinuclear system. The presence of two donor Fe$^+$ centres and one acceptor Fe$^{3+}$ centre is responsible of the intensity enhancement of a factor of two in the IVCT band of 55$^+$ over the (Fc–Fe$^+$) case.

Even if the central ferrocenyl unit is reasonably the first centre to be oxidized, as it bears two electron/donating substituents, the latter by a statistical factor of 2 ($\approx 50\%$), supporting valence localization (Class II) for the trinuclear system. The presence of two donor Fe$^+$ centres and one acceptor Fe$^{3+}$ centre is responsible of the intensity enhancement of a factor of two in the IVCT band of 55$^+$ over the (Fc–Fe$^+$) case.

In the case of the cation of bis(ferrocenyl) 57$^+$, the optical transition of Red–Ox yields Ox–Red and no adjustment in the iron–iron distance is required during the relaxation process. Conversely, for the cation of tris(ferrocenyl) 58$^+$, the transition from Red–Ox–Red to Ox–Red–Red should involve a modification of the internuclear distance and requires more energy than Red–Ox to Ox–Red transition in 57$^+$, not only for the energetic difference between different ground states but also for the tension resulting from the difference in iron–iron distances between Red–Ox, Red–Red and Ox–Ox combinations. 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.$^{70}$

Similar shifts to higher energy of the IVCT band caused by increasing the oxidation state were found in a series of linear oligo(ferrocenyldimethylsilanes) from two to nine ferrocenyl units prepared by Gieger and Manners (62–69).$^{71}$

Their $\Delta E$ splittings were not large enough to generate selectively the single mixed-valence states, due to weaker metal–metal interaction through the dimethylsilylene moiety. For oligomer systems containing an odd number of ferrocenyl groups, two reversible redox waves of varying intensities were observed, suggesting that two unresolved one-electron processes were present.

For the tris(ferrocenyl) 63 and the other systems with an even number of iron centres larger than two, three reversible redox processes of varying intensities were found.

As the chain length of both odd and even oligomers increased, only two reversible redox processes could be observed: alternating ferrocenyl sites are first oxidized, a situation which minimizes the electrostatic repulsion, and the iron sites in-between are oxidized at a higher potential. An X-ray diffraction study of tris(ferrocenyl) 63$^{73}$ supported this hypothesis.

Spectroelectrochemical experiments for partially oxidized oligo(ferrocenylsilanes) showed weak IVCT absorptions ($\nu_{\text{max}} = 7500–9000 \text{ nm cm}^{-1}$, $\epsilon_{\text{max}} < 150 \text{ M}^{-1}\text{ cm}^{-1}$) typical of class II mixed-valence species. The trimuclear 63$^+$ and binuclear 62$^+$ monocation displayed IVCT characteristics similar in energy, extinction coefficient and half-height bandwidth, resulting in a metal–metal coupling weaker than that of biferrocene.$^{72}$ In contrast to linear analogs, the CV and DPV of the related cyclic oligo(ferrocenyl-dimethylsilanes) from two to nine ferrocenyl units...
displayed two reversible redox processes for cyclic oligomers containing an even number of iron centres, while three reversible redox processes were observed for cyclic oligomers containing an odd number of iron centres.\textsuperscript{73} The results suggested that electrostatic interactions govern the stepwise oxidation of these macrocycles. The effect of an adjacent positive charge is stronger in the smallest and more constrained cycles containing two and three ferrocenyls, consistent with strong through-space interactions.

Other oligo- and poly(ferrocenyl) compounds containing an heteroatom in the bridge, such as tetraferrocenyldisiloxanediol, hexaferrocenyl-cyclotrisiloxane, poly(ferrocenylsulfide) and poly(ferrocenylselenide) were prepared by Manners.\textsuperscript{74} The CV studies were consistent with the presence of significant iron–iron interactions.

Very few electrochemical and spectroscopic studies have been reported on cyclic ferrocenyl triads in which rigid, two-dimensional C\textsubscript{2r}-arrays are defined by directly linking three cyclopentadienyl groups.

Bunz\textsuperscript{75} reported the preparation of the first organometallic dehydroannulenes (70 and 71). These cyclic conjugated triferrocene compounds could be assembled by directly linking cyclopentadienyl groups through butadiyne linkers to define a rigid cyclic array.

The electrochemistry of 70 and 71 was investigated. While \textit{anti} 70 displayed three sequential one-electron oxidation processes at 0.61, 0.74 and 0.83 V, indicative of the formation of detectable mixed-valence intermediates, \textit{syn} 71 exhibited only two waves at 0.61 and 0.78 V, involving one and two electrons, respectively. The observed splittings are relatively small, suggesting that electronic and electrostatic interactions are weak in these systems. Interestingly, the first oxidation potentials are identical, while the ∆E splittings between the first and second waves are different, 0.23 and 0.17 V, leading to the conclusion that, albeit the distance between ferrocenyl groups are relatively large, 70 and 71 display different electrochemical properties depending on the their geometry.

Unfortunately, the optical properties of the mixed-valence cations 70\textsuperscript{\textpm2} and 71\textsuperscript{\textpm2} were not reported.

We have recently reported the synthesis of the prototypical cyclic metallocene triads, namely the isomers \textit{syn,syn,anti-}[\{(FeCp)\textsubscript{3}\textsuperscript{+}\textsubscript{2}Td\} (72) and \textit{syn,syn,syn-}[\{(FeCp)\textsubscript{3}\textsuperscript{+}\textsubscript{2}Td\} (73) which can be figured out as the “fusion” of three ferrocenes into a rigid cyclic array.\textsuperscript{76–79} The CV oxidation of 72 in dichloromethane/\textit{n}Bu\textsubscript{4}NPF\textsubscript{6} proceeded in three one-electron steps, the first and second fully reversible at \(E_{1/2} = 0.23\) and 0.61 V vs. SCE, the third chemically irreversible and nondiffusion-controlled (\(E_p = 0.94\) V) with a typical stripping peak as its cathodic counterpart (Fig. 8).

The ∆E splitting between the first and second wave, as well as the related value of the comproportionation constant, is indicative of the thermodynamic stability of the cationic species 72\textsuperscript{+}\textsubscript{2} which could be generated by chemical oxidation and analysed at room temperature by optical spectroscopy.

![Fig. 8](image-url) CVs at different potential scan reversals of 72 in dichloromethane at Au disk electrode (d = 0.5 mm), scan rate \(v = 0.5\) V s\textsuperscript{-1}, \(T = 20\) °C. Reprinted with permission from \textit{Angew. Chem., Int. Ed.}, 2008, 47, 5331. Copyright 2008 John Wiley & Sons, Inc.

Gaussian deconvolution of the spectrum obtained in the NIR/IR region showed three IVCT bands at 3430, 5310 and 7030 cm\textsuperscript{-1} (Fig. 9).

Considerable complexity may be expected in the theoretical analysis of IVCT transitions in trinuclear complexes due to the presence of multiple electronically coupled redox centres. As the electronic coupling increases to almost delocalized and delocalized, the classical Hush model is no longer suitable and trimetallic complexes have been shown to manifest properties that are different from those of their related bimetallic systems\textsuperscript{116} due to the possibility of itinerant “extra” electron hopping over the coupled sites.\textsuperscript{77}

![Fig. 9](image-url) NIR/IR spectrum of the 72\textsuperscript{+}\textsubscript{2} cation in dichloromethane (straight line) and Gaussian deconvolution (dashed lines). Reprinted with permission from \textit{Angew. Chem., Int. Ed.}, 2008, 47, 5331. Copyright 2008 John Wiley & Sons, Inc.

More importantly, the influence of the third metal is such that within the three-site classical model the localized-to-delocalized transition is favoured relative to the two-site case,\textsuperscript{11a,b} although this effect were not been experimentally verified before.\textsuperscript{11e}

Remarkably, we provided rare experimental evidence that the introduction of a third metal centre increases the strength of the metal–metal interaction with respect to that of the structurally related binuclear systems.\textsuperscript{78}

The IVCT bands of 72\textsuperscript{+}\textsubscript{2} appeared at low energy, narrow and solvent-independent, as expected for an almost delocalized Class II–III mixed-valence system. In contrast, Class II behaviour was observed for the structurally related cations of the bimetallic [(CpFe)\textsubscript{2}(as-indacenediide)] isomers 74 and 75, previously prepared by some of us.\textsuperscript{78}
Tetra(ferrocenyl) complexes

Homoleptic tetra(ferrocenyl), EFc₄, derivatives of the Group 14 elements C, Si, Ge, Sn, and Pb have been prepared (76-80). SiFc₄, 77⁷⁹ and Sn[(C₅H₅)₂(C₅H₅CH₂NMe₂)₂Fe]₄, 8²⁰ have been prepared and fully characterized including investigation of electrochemical properties.

Cyclic voltammetry of 77 in benzonitrile showed four resolved and reversible oxidations waves with wave separations of 0.18, 0.14 and 0.10 V.

The spread of the four potentials over 420 mV indicated appreciable interactions among the ferrocenyl groups upon successively oxidation. Instead, a solution of 82 in dichloromethane/nBuNPF₆ was oxidized in three steps with splitting of 0.12 and 0.14 V in a 2e/1e/1e sequence.

The zwitterion BFc₄ 8¹⁶ provided four reversible one-electron oxidations with an even larger overall spread of 590 mV. Remarkably, 8¹, which contains one iron(III) and three iron(II) units, has been characterized as a mixed-valence system in solution with a broad IVCT band at 4550 cm⁻¹ and localized valences in the solid state.²²

Heinz²⁵ has isolated and fully characterized the substituted tetraferrocenylstannane Sn[(C₅H₅COOCH₃)₂(C₅H₅)Fe]₄ (8₃) which was oxidized in three steps to the tetracation in a 1e/1e/2e sequence with a splitting of 0.12 V each, suggesting some interaction. The lack of coplanarity of the redox-active subunits in the congested EFc₄ compounds indicated that through-space electronic communication occurs rather than through-bond. In these very crowded complexes, the metal–metal interaction is essentially due to electrostatic effect which is expected to be dominant in determining the value of the related comproportionation constant λ₂.

Stepwise oxidation of 8³ with AgSbF₆ in dichloromethane showed the appearance of an absorption band around 5000 cm⁻¹ assigned to an IVCT transition.

Its intensity increased up to 2–3 equivalents of oxidant added, indicating the formation of 8⁵ via 8³. The electronic coupling H in 8³ and 8⁵ (145 and 220 cm⁻¹, respectively) was estimated using the Hush relationship (eq. 6) with r = 6 Å (Δεmax = 4800, 4500 cm⁻¹, εmax = 125, 280 M⁻¹ cm⁻¹ and Δνmax = 3035, 3345), values typical of weakly coupled, class II, mixed valence cations.

A square of four electronically coupled sites containing two itinerant electrons is reasonably a useful building block for quantum cellular automata (QCA) devices. The first example of an isolated four-metal, mixed-valence complex containing two mobile electrons in a square geometry, i.e. CpCo(Fc₅)₂(8⁴), was fully characterized by Long and Fehlner,²⁶ a symmetrical square system containing two ferrocene and two ferrocenium moieties having properties suitable for use as a component for QCA circuits.

Though this system, based on the (η⁵-cyclobutadiene)(η⁵-cyclopentadienyl)Co platform (8⁴) was early described by Raush²⁶ and promising data for the 8⁴/2+/2+ relative to and IVCT bands in the visible and NIR region were reported, electrochemistry in dichloromethane/nBuNPF₆ was unsatisfactory and none of these ions were previously isolated.

The cations 8⁴⁺ and 8⁵⁺ were isolated and characterized. In particular, electrochemistry of 8⁴ and NIR spectra of 8⁴⁺ and 8⁵⁺ have been re-examined in a 1:1 mixture of CH₂Cl₂/CH₂CN. CV and SWV experiments in dichloromethane gave good resolution with evidence of three redox waves. In SWV, the unresolved wave at the most positive potential clearly evidenced the presence of a fourth peak (E1/2 = -0.09, 0.08, 0.23, and 0.28 V vs Fe/Fc⁺).

The bands observed for 8⁴⁺ and 8⁵⁺ were assigned to IVCT transitions, that of 8⁴⁺ occurring at higher energy. The solvent dependence of νmax and the Hush parameters calculated from the band energies, bandwidths, and intensities suggested electron localization, class II, behaviour in the Robin-Day classification.
In the solid state, two Fe\textsuperscript{II} and two Fe\textsuperscript{III} sites were observed in both the IR and Mössbauer spectra of 84\textsuperscript{3+} and 84\textsuperscript{2+}, indicating that these cations are valence trapped, class II, compounds on the 10\textsuperscript{-12} s IR time scale.

The valence trapping observed in the solid state suggests that 84\textsuperscript{2+} possesses properties that permit its use as a building block in molecular QCA cell.

A number of meso ferrocenyl porphyrins has been reported in literature.\textsuperscript{55} The tetra(ferrocenyl) substituted porphyrin (85) has been prepared and investigated by Nemykin and Galloni, and is undoubtedly a potential candidate for application in QCA device,\textsuperscript{41,86} and a photoactive material for photoelectrochemical cells.\textsuperscript{87}

The electrochemical properties of 85 were studied using CV, DPV and SWV methods in different combinations of solvent and supporting electrolyte.\textsuperscript{86c}

![Diagram](attachment:85.png)

In particular, resolution of the redox events was obtained by using the weakly coordinating nBu\textsubscript{2}NB(rCF\textsubscript{3})\textsubscript{4} as the supporting electrolyte in the low coordinating solvent dichloromethane. In this medium, the ferrocenyl-based oxidation resulted in four well separated one-electron oxidation processes at \(E_{1/2} = -0.07, 0.15, 0.24\) and 0.34 V vs Fe/Fc\textsuperscript{0}. The \(\Delta E\) splitting between the first two waves displayed the largest value with respect those between the subsequent ones; similar results but with less pronounced \(\Delta E\) splitting were observed in dichloromethane with the more coordinating nBu\textsubscript{2}NPF\textsubscript{6} electrolyte (\(E_{1/2} = -0.01, 0.08, 0.14\) and 0.25 V vs Fe/Fc\textsuperscript{0}).

The increased wave separations, observed when the weakly coordinating anion B(rC\textsubscript{6}F\textsubscript{5})\textsubscript{4}\textsuperscript{−} was present in the supporting electrolyte, could be ascribed to the existence of significant electrostatic repulsion between the non-coordinated cationic centres, especially in the dication 85\textsuperscript{2+}. On the other hand, the persistence of a \(\Delta E\) splitting in traditional electrolyte containing the anions BF\textsubscript{4}\textsuperscript{−} or PF\textsubscript{6}\textsuperscript{−}, which may react as nucleophiles with radical cations, corresponds approximately to the electronic communication in the absence of other significant factors.\textsuperscript{30a}

Two processes are conceivable for the formation of 85\textsuperscript{2+}, i.e. the oxidation of the second ferrocenyl group at an adjacent or opposite position relative to the first oxidized iron centre. Statistically, the oxidation of the adjacent substituent is more favoured. However, the electrostatic repulsion in the dication with the charges located at opposite positions should be reasonably less.

Spectroelectrochemical and chemical oxidation of 85 resulted in formation of the 85\textsuperscript{5+} and 85\textsuperscript{4+} mixed-valence species and of 85\textsuperscript{3+}. The IVCT bands observed in the NIR region for 85\textsuperscript{5+}, 85\textsuperscript{4+} and 85\textsuperscript{3+} were analysed using the Hush model; the magnitudes of the electronic coupling \(H\) were in agreement with the class II character in the Robin-Day classification and indicative of trapped-valency. Valence localization of 85\textsuperscript{5+} and 85\textsuperscript{4+} was also confirmed by MIR, Mössbauer and XPS data.

These remarkable properties prompted Galloni and Niemykin’s groups to prepare and characterize novel tetra(ferrocenyl)porphyrin containing self-assembled monolayers (SAMs), and a preliminary investigation on their photocurrent generation efficiency.\textsuperscript{88}

The electrochemical and optical properties of tetra(ferrocenyl) substituted thiophene, furan and pyrrole 86\textsuperscript{86–89} were prepared and investigated by CV, SWV and in situ UV–vis/NIR spectroscopy by Lang.\textsuperscript{43b–e}

As the iron–iron distances in this series are almost equal, the electrostatic contribution to the \(\Delta E\) separation was found comparable and, consequently, the trend of \(\Delta E\) corresponded to the electronic communication.

The \(\Delta E\) values between the first and the second redox waves followed the same trend observed in the bis(ferrocenyl) heterocycles 16–19. However, as evidenced from solid state structure of 88, the lack of coplanarity with the heterocyclic bridge due to the higher steric hindrance of the adjacent ferrocenyl groups in 86–89 caused the decrease of \(\Delta E\) values with respect to the bis(ferrocenyl) analogues. The separation of the successive redox events is mostly attributed to electrostatic effects.

The appearance of IVCT absorptions in the NIR region confirmed the existence of electronic coupling in the corresponding mono- and dicationic species and all mixed-valence compounds, except the class I thiophene-based 86\textsuperscript{71}, were classified as class II systems according to Robin and Day.

The \(\Delta E\) values between the first and the second redox waves correlated with the communication of the iron centres, namely the oscillator strength \(f\) of the IVCT transitions found in NIR region for 86\textsuperscript{86–89} (eq. 17 and 18), and allowed to estimate the electron transfer distance \(r\), as for the series bis(ferrocenyl) heterocycles 16–24. The electronic coupling in tetraferrocenyl heterocycles 86\textsuperscript{86–88} was found much lower than that observed in the bis(ferrocenyl) derivatives 16–18. This could be attributed to the decreased coplanarity of the ferrocenyl groups with the central heterocycles due to the higher steric demand in the more crowded 86\textsuperscript{86–88} series.

Electrochemical and optical investigations on linear tetra(ferrocenyl) systems were reported by Meyer\textsuperscript{58} (56), Nishihara\textsuperscript{59} (59) and Geiger\textsuperscript{64} (64) (see the discussion in the previous Section). The position of the subsequent positive charges and the electrochemical characteristics in the mono and polycationic species depended on the interplay of the electrostatic and energetic factors along the chain of these multi(ferrocenyl) oligomers. In all the cases for which an absorption band was observed in NIR region, the typical characteristics of Class II mixed-valence complexes were observed.
Penta(ferrocenyl) complexes

Penta(ferrocenyl) complexes are quite rare due to synthetic difficulties.

Linear penta(ferrocenyl) complexes 60 and 65 displayed electrochemical and optical behaviour quite similar to that found along the corresponding series of compounds with increasing number of concatenated ferrocenyl groups (see the discussion in the previous Section).

Vollhardt synthesized and characterized the first “star-shaped” oligocyclopentadienyl metal complexes, among which the penta(ferrocenyl) derivatives 90–92.\(^\text{90–92}\)

The lack of coplanarity of the central cyclopentadienyl, evidenced by the X-ray structure, attenuates but does not remove intermetallic interaction in 90, as indicated by CV data in CH\(_2\)Cl\(_2\) / nBu\(_4\)NPF\(_6\), which displayed three oxidation waves at \(E_{1/2} = 0.05, 0.17\) and 0.28 V vs Fe/Fe\(^+\) in a 2e/1e/1e sequence.

Compared to 90, the molecule of 91 is much released of strain. Nevertheless, the ferrocenyl bonded to the sp\(^3\)-carbon is oriented out of the mean plane of the cyclopentadiene. Comparison of the CV data \((E_{1/2} = -0.11, 0.17$$ and $$0.33$$ V) with that of 90, clearly revealed the effect of isolating electronically the sp\(^3\)-bonded ferrocenyl from the rest of the molecule.

The anion 92 showed three oxidation steps at \(E_{1/2} = -1.25, 0.20\) and 1.20 V, reflecting the transitions anion \(\rightarrow\) radical \(\rightarrow\) cation (possibly ferrocenyl centred) \(\rightarrow\) dication.

Similarly to what observed in the very crowded EFc\(_4\) complexes, we believe that the metal–metal interaction is essentially due to electrostatic effect. Unfortunately, neither the effect of the weakly coordinating nBu\(_4\)NB(C\(_6\)F\(_5\))\(_4\) on the wave multiplicity and separation, or the presence of mixed-valence cations were verified.

The advances in manipulation of single molecules\(^\text{89}\) have stimulated much interest in the synthesis of molecular machines,\(^\text{91–93}\) nanowheels,\(^\text{91}\) nanocars,\(^\text{92}\) and nanogears.

Recently, Rapenne and Launay reported the synthesis of ruthenium(II) 1,2,3,4,5-penta(p-ferrocenylyphenyl)-cyclopentadienyl-hydrotris(indazolyl) borate (93), a piano stool complex described as the active part of a potential organometallic molecular machine, i.e. a rotor composed by five terminal ferrocenyl groups connected to a tripodal ligand (stator) by means of a ruthenium(II) centre. This system may be considered as the heart of a future molecular motor.\(^\text{94}\)

In 93 there is essentially one degree of freedom: the rotation of the upper part with respect to the lower one. All the requirements for such a molecule to operate as a molecular motor were verified: (i) within CV experiments in CH\(_2\)Cl\(_2\) containing nBu\(_4\)NPF\(_6\), the reversible oxidation potential of ferrocenyl groups occurred at the same potential (0.52 V vs SCE), lower than that of the ruthenium centre (0.82 V vs SCE) which consequently remains inert towards the redox cycles of the terminal ferrocenyl groups; (ii) no IVCT band was observed by spectroelectrochemistry in the vis-NIR region, showing that the electrostatic interaction and electronic coupling between two adjacent metal centres are absent or very weak.

Hexa(ferrocenyl) complexes

Electrochemical and optical investigations on linear hexa(ferrocenyl) systems were reported by Nishihara\(^\text{89}\) (59) and Geiger\(^\text{71}\) (66) and discussed in the previous Sections.

As far as “star-shaped” hexaferrocenyl complexes are concerned, Vollhardt was able to synthesize the elusive for decades hexaferrocenylenzene (94).\(^\text{95}\)

The six bulky ferrocenyl groups give the molecule an extremely crowded structure, as evidenced by X-ray analysis. The C\(_6\)H\(_4\) substituents deviate considerably from coplanarity with the benzene ring, with dihedral angles falling into two alternating groups averaging of 30.8 and ~81.9\(^\circ\). In addition, the benzene ring adopts a chair conformation caused by the perferrocenylation.

The CV in CH\(_2\)Cl\(_2\) / nBu\(_4\)NPF\(_6\) exhibited well separated redox waves at \(E_{1/2} = -0.16, -0.03\) and 0.22 V vs Fe/Fe\(^+\) in a 1e/2e/3e sequence. Taking into account the lack of planarity and the close proximity of...
the ferrocenyl groups, we believe that the separation of these redox events is mostly owed to electrostatic effects. Regrettably, the effect of the weakly coordinating \(n\text{Bu}_4\text{NBAr}_4^+\) and the existence of mixed-valence states were not examined.

A family of rigid “star-shaped” ferrocenyl-terminated complexes has been synthesized by Astruc, including hexa(ferrocenylethynyl)benzene complexes (95), also containing permethylated (96) and monomethylated (97) cyclopentadienyl ligands.\(^{50}\)

The CVs of 95–97 in \(\text{CH}_2\text{Cl}_2\) showed a single wave when \(n\text{Bu}_4\text{NPF}_6\) was used as the supporting electrolyte, as well the CVs of the structurally related bis(ferrocenyl) 6p and tris(ferrocenyl) 47 complexes.

The lack of wave splitting \(\Delta E\) was attributed to the absence of significant intramolecular communication between the ions. The CVs were also recorded with \(n\text{Bu}_4\text{NBAr}_4^+\) as supporting electrolyte, whose advantages were discussed above. While the CV of the binuclear 6p still showed a single wave, those of the trinuclear 47 and hexanuclear 95 split into three well-separated one-electron and two-electron waves, respectively, meaning that the splitting might not result from electronic communication among the redox centres but from electrostatic effects due to the scarce ion pairing capability of \(\text{BAr}_4^-\) towards the oxidized compound with respect to traditional anions.

The electrostatic effect suggested the distinction among the three two-electron oxidation steps of 95 on the basis of the large differences of the electrostatic interaction in the \textit{ortho}, \textit{meta}, and \textit{para} positions (Fig. 10).

The CV of 96 with \(n\text{Bu}_4\text{NBAr}_4^+\) resulted in a broad overlap of not resolved waves. Interestingly, the CV of the monomethylated 97 was more clearly resolved and six single-electron oxidation waves could be distinguished. This result was attributed to the perturbation of the ion-pairing strength by the presence of a single methyl group on each ferrocenyl redox centre.

The lack of spectroscopic studies on the mixed-valent behaviour of the cationic derivatives prevents any ultimate conclusion on the nature, electrostatic and/or electronic, of the metal–metal interaction.

Recently, the hexametallic dendrimer (98)\(^{3c}\) and the 1,3,5-tris(ferrocenylethynyl) benzene (99)\(^{3e}\) were successfully synthesized by Astruc.

The CV of 98 in \(\text{CH}_2\text{Cl}_2/\text{nBu}_4\text{NPF}_6\) showed a fully chemically and electrochemically reversible six-electron wave. Contrary to the case of the hexa(pentamethylferrocenylethynyl)benzene 96, no electrostatic effect was observed using \(n\text{Bu}_4\text{NBAr}_4^+\) as the supporting electrolyte, due to the more distant position of the redox groups from one another in 98.

The presence of three biferrocenyl units in 99 introduced electronic effects responsible for mixed-valence stabilization and localization, observed by CV, Mössbauer, IR and NIR spectroscopic.
the octanuclear \{1,3-di(biferrocenylethynyl)-5-ethynylbenzene\}. At difference, in the case of the tetranuclear bis(biferrocenyl)bis(ethynyl) derivative, the use of \(n\)Bu_{4}NBAr_{4} as completely changed the CV and stabilized the mixed-valent species with respect to the standard electrolyte \(n\)Bu_{4}NPF_{6}. In fact, larger \(\Delta E\) between the first and second waves of the biferrocenyl units was observed, i.e. larger comproportionation constant. The electrostatic effect is much stronger than for 99 because the bis(ethynyl) linker is much shorter than the bis(ethynyl)arene linker. The electrostatic contribution is not observed with \(n\)Bu_{4}NPF_{6}.

The hexa(\(p\)-ferrocenylphenyl)benzene (100) was prepared by Chehny\(^99\)

The CV of 100 in CH_{2}Cl_{2} and \(n\)Bu_{4}NPF_{6} as the supporting electrolyte showed only a single reversible wave. Redox titration confirmed that it ejects six electrons at the same potential. The incremental addition of the naphthalene cation radical as a robust one-electron oxidant afforded the bright green hexacation 100\(^{3+}\) which showed a band in the NIR region \(\nu_{\text{max}} = 9050 \text{ cm}^{-1}, \epsilon_{\text{max}} = 1400 \text{ M}^{-1} \text{ cm}^{-1}\) in dichloromethane, typical of a ligand-to-metal charge transfer (LMCT) transition.

The authors suggested that the ferrocenyl groups are not electronically coupled. However, the use of the weakly coordinating \(n\)Bu_{4}NB(C_{6}F_{5})_{4}, which may be able to separate the single oxidation steps allowing to the existence of mixed-valency and IVCT bands, was not considered.

The last proposed molecules of this tracking shot on the multi(ferrocenyl) family are the 3,3',4,4',5,5'-hexaferrocenyl-2,2'-bithiophene (101) and the related 3,4,5-tris(ferrocenyl)thiophene (102), recently prepared by Lang\(^{43a,100}\).

Their electrochemical and electronic properties were defined by CV and SWV measurements and in situ UV−vis/NIR spectroelectrochemistry. Three successive one-electron oxidation at \(E_{1/2} = -0.12, 0.15\) and 0.43 V vs Fe/C_{6}F_{5} were observed for the trinuclear 102 in dichloromethane solutions using \(n\)Bu_{4}NB(C_{6}F_{5})_{4} as supporting electrolyte. The hexanuclear 101 displayed five redox processes at \(E_{1/2} = -0.165, 0.26, 0.49, 0.65\) and 0.80 V vs Fe/C_{6}F_{5} in anisole/\(n\)Bu_{4}NB(C_{6}F_{5})_{4}, the first one corresponding to two one-electron events close together followed by four separated one-electron waves. Stepwise oxidation of the ferrocenyl groups was observed with spectroelectrochemistry. Surprisingly, while 102\(^{2+}\) and 102\(^{3+}\) lead to the appearance of an IVCT absorption band at 6628 cm\(^{-1}\) and 7520 cm\(^{-1}\), respectively, with characteristics typical of a mixed-valent Class II system, the absence of low-energy bands in the NIR region for 101\(^{4n}\) \((n = 1–5)\) indicated that the ferrocenium units essentially communicate electrostatically with each other, and the positive charges are mainly localized on the ferrocenium moieties, similarly to what found for the supercrowded tetraferrocenyl thiophene cation 86\(^{+}\).

Conclusions

The aim of this review is that to provide a perspective on the family of multi(ferrocenyl) complexes with a number of ferrocenes from two to six. In particular, for molecules with more than two metal groups, three molecular shapes were considered, namely star, linear and cyclic systems.

Specifically, we have focused our attention on those key complexes which were employed as precursors of mixed-valence cations displaying mainly electrostatic and electronic interactions that in some cases cooperate in determining the overall metal−metal communication. We have tried to identify the experimental approaches principally employed to highlight the contribution of these two effects, and here summarized with some warnings and “precautions for use”:

- the thermodynamic stability of the mixed-valence state can be easily calculated from electrochemical data; larger and resolvable \(\Delta E\) between successive redox events are indicative of increased \(K_s\) values;
- the \(\Delta E\) splitting between two CV waves of two equivalent redox centres, observed using traditional supporting electrolyte containing BF_{4} and PF_{6} which may react as nucleophiles with radical cations, could correspond approximately to the electronic communication in the absence of other significant factors, but undetectable or small \(\Delta E\)s are not diagnostic of a negligible communication;
- if \(\Delta E\) splitting or increased wave separation are observed with supporting electrolytes containing weakly coordinating anions such as B(C_{6}F_{5})_{4}, these effects may be attributed to significant electrostatic repulsion between the positive charges in the dication;
- warning is needed in the interpretation of electrochemical data due to the dependence of \(\Delta E\) splitting on the nature of the solvent and supporting electrolyte; more diagnostic are optical investigations in the NIR region where mixed-valence species typically absorb.

Many fascinating examples of multi(ferrocenyl) complexes are reported in literature, a few of which are promising candidate for application as molecular devices such as quantum cellular automata or sensors. In this perspective, the experimental validations summarized above and described by several studies here reviewed represent the minimal requisites for the best comprehension of the nature of the metal−metal interaction.
Acknowledgements

Financial support by Italian MIUR (ex-60% grants) is gratefully acknowledged.

Notes and references


44 A. Hildebrandt and H. Lang, Organometallics, 2013, 32, 5640.


85 For a comprehensive literature, see 42 and reference therein.


