Key Multi(Ferrocenyl) Complexes in the Interplay between Electronic Coupling and Electrostatic Interaction

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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 nature of the bridging ligand, the distance among the redox-active centres and the medium affect the electronic and electrostatic properties of the molecules.

Introduction

The preparation of multicomponent molecular systems with specific redox, optoelectronic, magnetic, and conductive properties is currently fundamental for modern technology. 1

Among metallocene-based metallicorganic structures, 2 multi(ferrocenyl) compounds were suggested as potential candidates for molecular electronics due to their well-defined and robust redox properties. 3

Indeed, multi(ferrocenyl) complexes with conjugated spacer groups and displaying multielectron redox chemistry are of particular interest owing to their characteristics due to unpaired electron density migration properties of their mono-oxidised derivatives. 4 These switchable arrays were intensely studied because conjugated organic chains containing Fe II/FeIII couples of the ferrocenyl group can be potentially used as quantum cellular automata, optoelectronic materials for application in redox or photonic devices. 5

Many of these ferrocenyl derivatives belong to the family of mixed-valence complexes in which at least two equivalent ferrocenyl units electronically interact and the Fe II/FeIII oxidation states coexist in the same molecule. The mixed-valence systems are excellent benchmarks for the investigation of the electronic interactions. 6 Actually, in multi(ferrocenyl) complexes the formation of mixed-valence intermediates is often responsible for the aforesaid properties.

The synthesis of the Creutz-Taube 7 mixed-valence ions encouraged the investigations on a series of coordination complexes in order to establish the way in which two or more metals linked by nitrogen (or other heteroatoms) containing bidentate ligands. 8

Concomitantly, Cowan and co-workers focused their research on different diferrocenyl complexes, 9 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. 10 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 11 and the classical Marcus-Hush theory. 12

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 M₁ to M₂ occurs and vice versa (eq 1):

\[ M_1^{+} + M_2^- \rightarrow M_1^- + M_2^+ \]  

(1)

The accessibility of the charge delocalized transition state (or excited state) allows the occurrence of the intercalation 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):

\[ \overset{\text{M1}^{+} \cdot \cdot \cdot \text{M2}^{-}}{\text{M1}^{-} \cdot \cdot \cdot \text{M2}^{+}} \leftrightarrow \overset{\text{M1}^{-} \cdot \cdot \cdot \text{M2}^{-}}{\text{M1}^{+} \cdot \cdot \cdot \text{M2}^{+}} \]  

(2)

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).13

Intramolecular metal-to-metal electron transfer can be theoretically inspected using the classical model introduced by Marcus.12-14 According to Marcus, the potential energy surface of a degenerate mixed-valence system can be described by two parabolic curves, \( G_\lambda = \lambda q^2 \) and \( G_\theta = \lambda(1-q)^2 \), which represent the non-interacting (diabatic) states as a function of a global reaction coordinate “q”.

The electronic coupling of these 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.

![Fig. 1 The adiabatic \((G_1\) and \(G_2\), solid lines\) and diabatic energy surfaces \((G_\lambda \) and \(G_\theta\), dashed line\) for (a) localized class II and (b) delocalized class III systems for an isoergonic complex. \(\Delta G' = \Delta G / 2\) represents the resonance free energy per mixed-valence complex, where \(\Delta G\) accounts for the free energy of resonance exchanges.](image)

The two metal groups represent the donor and the acceptor, i.e. the two sites between which electron transfer occurs, and they are connected by an organic spacer (or bridging ligand); the molecule is surrounded by a solvation sphere, the equilibrium polarization of which is generally different before and after the electron transfer. The energy cost due to geometry modifications to go from a neutral to a charged metal centre (and vice versa) is called reorganization energy, \(\lambda\).

Hush applied the Marcus theory to the issue of intercalation transitions.12a-c, 14 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 \(H\):

\[ G_1 = \frac{1}{2} \{(G_\lambda + G_\theta) - [(G_\lambda - G_\theta)^2 - 4H^2]^{1/2}\} \]  

(3a)

\[ G_2 = \frac{1}{2} \{(G_\lambda + G_\theta) + [(G_\lambda - G_\theta)^2 - 4H^2]^{1/2}\} \]  

(3b)

For a weakly coupled Class II system, when the surface splitting is smaller than the reorganization energy \((2H \ll \lambda)\), 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 \(\Delta G^0\) given by eq. 4:

\[ \Delta G^0 = \frac{\lambda^2}{4} - H + \frac{H^2}{\lambda} \]  

(4)

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 \(\Delta G^0\); (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 intervalence charge transfer (IVCT) absorption in near infrared (NIR) region. The maximum energy of this IVCT transition is \(\tilde{\nu}_{\text{max}} = \lambda\) 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 \((2H \gg \lambda)\), the resulting adiabatic ground-state surface displays a single minimum and \(\Delta G^0\) disappears at \(H = \lambda/2\), as predicted by eq. 4. The odd electron is now delocalized between the metal centres and \(\tilde{\nu}_{\text{max}} = 2H\) (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 intervalence band is predicted to be dependent of \(\Delta G^0\) (eq. 5):

\[ \tilde{\nu}_{\text{max}} = 4\Delta G^0 \]  

(5)

The magnitude of \(H\) is related to the maximum energy \(\tilde{\nu}_{\text{max}}\) the molar absorption coefficient \(e_{\text{max}}\), the half-bandwidth \(\Delta \tilde{\nu}_{\text{max}}\) of the IVCT absorption, and the true electron transfer distance \(r\):

\[ H = \frac{0.0206}{r} \sqrt{\tilde{\nu}_{\text{max}} \Delta \tilde{\nu}_{\text{max}} e_{\text{max}}} \]  

(6)

When the electronic coupling is pronounced, \(r\) can be considerably shorter than the geometric distance \(r_0\). The value of \(\Delta \tilde{\nu}_{\text{max}}\) for a localized mixed-valence system is predicted by eq. 7,

\[ \Delta \tilde{\nu}_{\text{max}} = \sqrt{4RT \ln 2 \tilde{\nu}_{\text{max}}} \]  

(7)
that at the limit of high temperature \( (H >> k_BT, T = 298\, \text{K}) \) gives eq. 8:
\[
\Delta \tilde{\nu}_{1/2} (\text{cm}^{-1}) = \sqrt{2310 \, \tilde{\nu}_{\text{max}}}
\] (8)

Two fundamental reviews on the application of Hush theory to mixed-valence complexes of transition metal centres are those by Creutz\(^{15}\) and by Crutchley\(^{16}\). Eq. 7 and 8 are valid only for Gaussian-shaped bands and a rigorous quantum chemical formulation was given by Cave, Newton and Sutin\(^{17}\).

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 mean of eq. 7. If the values are similar, the valence state is considered class II; if the experimental bandwidth is smaller, it is class III.\(^{15,16,18}\) In addition, the effect of solvent on the mixed-valence properties has often been used to distinguish between class II or III complexes.\(^{1,2}\) In fact, if the rate of the electron transfer between donor and acceptor is smaller than the rate of solvent relaxation \( (10^{12}\, \text{s}^{-1}) \), \( \tilde{\nu}_{\text{max}} \) is predicted to be linear with the solvent parameter \((1/n^2 - 1/\varepsilon)\) by the classical two-state Hush theory.\(^{12,12}\) A blue shift of the band energy of a class II mixed-valence derivative is experimentally observed by increasing the quantity \( 1/n^2 - 1/\varepsilon \) and the odd electron is trapped on one metal. Conversely, the energy of the intervalence transition of a class III system is expected to be solvent-independent.

More recently, Meyer\(^{19}\) has defined borderline class II/class III systems which exhibit both localized and delocalized behaviours. Meyer stated that, if the rate of the electron transfer is greater than the rate of solvent relaxation, \( \tilde{\nu}_{\text{max}} \) of the mixed-valence complex appears solvent independent even though the odd electron is trapped on one metal in the electronic time scale \( 10^{13}\, \text{s}^{-1} \). For a borderline Class II/Class III mixed-valence species, when the thermal barrier \( \Delta G^2 \) is vanished and \( \tilde{\nu}_{\text{max}} = \lambda \), the electronic coupling \( H \) is equal to \( \tilde{\nu}_{\text{max}}/2 \).

Brunswig, Creutz and Sutin proposed a criterion based on the observed and calculated half-bandwidths,\(^{14b}\) according to eq. 9:
\[
\Gamma = 1 - \frac{(\Delta \tilde{\nu}_{1/2})_{\text{obs}}}{(\Delta \tilde{\nu}_{1/2})_{\text{calcd}}}
\] (9)
The value of \( \Gamma \) aids in classifying a mixed-valence species: for weakly coupled class II systems \( 0 < \Gamma < 0.1 \), for moderately coupled class II systems \( 0.1 < \Gamma < 0.5 \), for borderline class II/class III systems \( \Gamma \approx 0.5 \), and for delocalised class III systems \( \Gamma > 0.5 \).

2. Electrochemistry

Besides the optical techniques, electrochemistry is a powerful tool to inspect on the thermodynamic stability of mixed-valence systems and is frequently employed to predict the magnitude of metal-metal electronic interaction.

The thermodynamic stability of the mixed-valence state can be easily calculated from electrochemical data. The comproportionation constant \( K_c \) for the equilibrium described by eq. 10 is given by \( K_c = \exp(\Delta G_e/RT) \) where \( \Delta G_e \) is the oxidation potential difference between the first and second oxidation of a bimetallic complex measured by mean of cyclic voltammetry (CV), differential pulse voltammetry (DPV) and square wave voltammetry (SWV).

\[
\text{M}_1^{\text{+}+}\text{M}_2^{\text{+}+} \leftrightarrow \text{M}_1^{\text{+}+}\text{M}_2^{\text{+}+} \leftrightarrow 2 \text{[M}^{\text{+}+}\text{M}_2^{\text{+}+}]^{\text{+}+}
\] (10)

The nature of the spacer connecting two or multiple redox units has a relevant role in modulating \( \Delta G_e \) separations.

Larger and resolvable separations are indicative of increased \( K_c \) values, corresponding to greater thermodynamic stability of the mixed-valence state. The determination of the \( \Delta G_e \) value allows evaluating the related stabilization energy \( \Delta G_e = -F \Delta E \). Different energy factors contribute to the magnitude of \( \Delta G_e \):
\[
\Delta G_e = -F \Delta E = \Delta G_i + \Delta G_c + \Delta G_d + \Delta G_r + \Delta G_{ex} + \Delta G_{ip}
\] (11)

According to Sutton and Taube\(^{20}\), for most of mixed-valence complexes the first four factors mainly contribute to the magnitude of \( \Delta G_e \). In eq. 11, \( \Delta G_i \) reflects the statistical distribution of the comproportionation distribution: in an electrochemical experiment with a molecule containing \( n \) noninteracting equivalent redox centres, one should observe a separation of \((RT/F)\ln(2n)\) (for \( n = 2 \)) \( \Delta E = 36\, \text{mV} \), \( \Delta G_i = 4 \), \( \Delta G_c = 3.5\, \text{kJ} \) at 298 K\(^{21}\) a rather smaller value than that measurable with the common electrochemical techniques. \( \Delta G_c \) represents the electrostatic repulsion of two charge metal centres, \( \Delta G_i \) is the inductive factor dealing with the competitive coordination of the bridging ligand by the metal ions, and \( \Delta G_r \) accounts for the free energy of resonance exchanges, the only contribution to \( \Delta G_i \) denoting real metal-metal coupling. Sutton and Crutchley\(^{8} \) pointed out early that another term, \( \Delta G_{ex} \), 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 \( \Delta G_{ex} \) should be small or insignificant. Finally, Geiger has shown that ion pairing can have a strong effect on \( \Delta G_i \) and the ion-pairing factor \( \Delta G_{ip} \) either increases or decreases its magnitude depending on the charge of the complexes in eq. 10. The magnitude of \( \Delta G_e \) 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 nucleophility or ion-pairing ability of the supporting electrolyte can dramatically modify \( \Delta G_i \).

The importance of the electrostatic interaction was demonstrated by Sutton and Taube\(^{20}\) 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 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.

The dependence of \( K_c \) on metal-metal distance was discussed by Hush.\(^{24}\) When the metal centres are separated by a large distances, \( K_c \) becomes smaller and becomes 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/\( r_g \) (where \( r_g \) is the geometric distance) should be linear and pass through \( K_c = 4 \) for 1/\( r_g \to 0 \).

The only factor of \( \Delta G_{ex} \) which accounts for “real” metal-metal coupling is \( \Delta G_i \). We can break down \( \Delta G_{ex} \) into two contribution (eq. 12), \( \Delta G_{ex} \) which include all the nonresonance factors, and the resonance free energy \( \Delta G_r \):
\[
\Delta G_{ex} = \Delta G_{nr} + \Delta G_r
\] (12)
In the case of a symmetrical weakly coupled class II complex, it has been shown that the resonance stabilization is given by eq. (13):

$$\Delta G_r = \frac{2H^2}{\lambda} = \frac{2\lambda^2}{v_{\text{max}}}$$  \hspace{1cm} (13)

For a class III complex $\Delta G_r$ is predicted by eq. 14:

$$\Delta G_r = 2(H - \lambda/4) = \frac{v_{\text{max}} - \lambda}{2}$$  \hspace{1cm} (14)

It obviously results that $\Delta G_r = \frac{v_{\text{max}}}{2}$ for a borderline system $(H = \lambda)$ and $\Delta G_r \rightarrow v_{\text{max}}$ for very strongly coupled systems $(H \gg \lambda)$.

**Bis(ferrocenyl) complexes**

The series of bis(Ferrocenyl) polyenes of general formula Fe(CH−CH)₆Fe (1a−e, n = 1−6), prepared by Launay and Spangler, offered a unique opportunity to study accurately the intervalence electron transfer and the decay law of the electronic interaction with distance. The study of the mixed-valence species obtained by monoxidation of 1a−e showed that intervalence transition appeared at markedly low energy, and metal–metal electronic coupling existed even when the $\Delta E$ splitting was not observed (n = 4−6).²⁶

![1a-e: n = 1-6](image)

As expected, a plot of $\ln K_c$ vs $1/r_g$ was found linear and passed through $K_c = 4$ for $1/r_g \rightarrow 0$ (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,²² the Hush model allows $H$ to be calculated from the parameters of the deconvoluted intervalence band (eq. 6).

![Fig. 2](image)

**Fig. 2** (a) Comproportionation constant $K_c$ (log scale) as a function of $1/r_g$: (●) from redox titration; (X) from wave splitting. (b) Metal-metal coupling (log scale) $H$ as function of $r_g$ in the hypothesis of a trans configuration of terminal ferrocene groups.

From McConnell’s theory,²⁷ the coupling should decrease exponentially as $n$ increases according to eq. 15:

$$H_n = H_0e^{-\gamma n}$$  \hspace{1cm} (15)

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.

The isomeric complexes $E$ (2b) and $Z$,1-,2-bis(1’-ethyl-1-ferrocenyl)-1,2-dimethylethylene (3b) were reported by Dong and Peng. The complexes 2 and 3 provided the opportunity to study the intervalence electron transfer between two ferrocenyl groups as a function of the relative orientation and separation of donor and acceptor. However, the surprisingly similar optical properties found for weakly coupled 2b and 3b mixed-valence isomers, together with the electrochemical measurements of 2b and 3b, indicated that electron transfer is associated with $E=Z$ isomerization. Indeed, the solutions obtained by chemical reduction of the dioxidized cations and of the mixed-valence solutions showed both $E$ and $Z$ isomers. The isomerization was not observed in a solution of neutral complexes. Possibly, the isomerization is associated with thermal electron transfer or photoinduced electron transfer through the π* orbital of ethene bridge in mixed-valence or dioxidized cations.

![Fig. 3](image)

**Fig. 3** Structures of (a) 2a, (b) 1a, (c) 3a, and (d) 4a. 

In order to circumvent isomerization problems, the complexes 2a and 3a and the related 1,2-diferrocenyl-cyclooxene (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 $2a^\ddagger$, $3a^\ddagger$, and $4^\ddagger$, 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.²⁸

![Fig. 4](image)

**Fig. 4** Structures of (a) 5o, (b) 5m, and (c) 5p.

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,²⁹ Δ$E$ 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 ($131 \text{ mV}$), 5p ($104 \text{ mV}$) and 5m* ($90 \text{ cm}^{-1}$), 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* ($347 \text{ cm}^{-1}$) > 5o* ($202 \text{ cm}^{-1}$) > 5m* ($161 \text{ cm}^{-1}$). 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(ferrocenyli)ethynylbenzenes was carried out by Astruc$^{29}$ in order to get insight into the electrostatic or resonant nature of the interaction between ferrocenyI groups.

![Diagram of 6o, 6m, and 6p](https://example.com/diagram.png)

Previously, 1-bromo-3,5-bis(ferrocenylethynyl)benzene was reported by the Long and Zanello$^{30}$, 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 $n$Bu$_4$NPF$_6$ as the supporting electrolyte.$^{31}$

Weakly coordinating anions with highly delocalized negative charge, such as B(C$_6$F$_5$)$_4$, allow minimization of nucleophilic attack on the radical cations. In addition, they undergo much weaker ionic interaction, the largest values are obtained in less polar solvents with low donor number.$^{22}$ 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$^{22a,14b,23}$ and from electrochemical studies are frequently in poor agreement.$^{22}$ 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,$^{33}$ 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 $n$Bu$_4$NPF$_6$ as the supporting electrolyte, to two successive one-electron transfers with $n$Bu$_4$NB(C$_6$F$_5$)$_4$.

![Diagram of 7a and 7b](https://example.com/diagram.png)

Despite the small $\Delta E$ values even in the presence of $n$Bu$_4$NB(C$_6$F$_5$)$_4$, resolved by square wave voltammetry (Fig. 3), generation by chemical oxidation of the mixed-valence diiron cations and their characterization by optical spectroscopy were accomplished. Hush analysis of the IVCT bands in the NIR region indicated that 7a$^+$ and 7b$^+$ are Class II, moderate coupled, mixed-valence systems.

![Graph of Potential (V vs SCE) vs. Oxidation State](https://example.com/graph.png)

**Fig. 3.** Oxidative CVs in dichloromethane at 20 °C of 7a with (a) 0.1 M $n$Bu$_4$NPF$_6$, (b) 0.1 M $n$Bu$_4$NB(C$_6$F$_5$)$_4$, (c) DPV with 0.1 M $n$Bu$_4$NB(C$_6$F$_5$)$_4$. Oxidative CVs in dichloromethane of 7b with (d) 0.1 M $n$Bu$_4$NPF$_6$, (e) 0.1 M $n$Bu$_4$NB(C$_6$F$_5$)$_4$, (f) DPV with 0.1 M $n$Bu$_4$NB(C$_6$F$_5$)$_4$.

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 as-indacene in transmitting charge from the ferrocene to the ferrocenium terminal groups. Similarly, as previously reported by Coudret and Launay,$^{34}$ a single wave was observed for the bis(ferrocenyl)anthracene complex 8 and its TCNE.

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adduct 9 at the same potentials, corresponding to two close mono electrónico processes.

DPV allowed the resolution of the two processes and the determination of the $\Delta E$ and $K_c$ 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 intervalence 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 did not vanish despite the loss of conjugated character.

In its early works, Rausch described the synthesis of a series of compounds where up to four ferrocenyl groups are introduced on the cyclobutadiene ring of ($\eta^1$-cyclobutadiene)($\eta^1$-cyclopentadienyl)Co, among which the two bis(ferrocenyl) isomers cis-CpCo(Fc2Ph3C4) (10a) and trans-CpCo(Fc2Ph3C4) (10b) were examined with the aim to inspect the effect of positional isomerism on the properties of the mixed-valence species 10a+ and 10b+.

Within CV experiments in dichloromethane containing $n$Bu4NPF6 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 dioxidized forms of the two isomers gave rise to a band in the NIR region (10a+, $\tilde{\nu}_{max} = 8000$ cm$^{-1}$; 10a2+, 8930; 10b+, 6950; 10b2+, 9260) characterized by position, intensity, bandwidth, and solvent dependence typical of ICT bands of class II mixed-valence species. Since an iron–iron coupling is not possible in the dications, the authors proposed that the intervalence transition arose predominantly from a Co(I)-Fe(III) coupling. This hypothesis was corroborated by the observation that the cation of the monoferrrocenyl CptCo(FcPh3C4) exhibited a band in NIR region ($\tilde{\nu}_{max} = 7840$ cm$^{-1}$) similar to those seen for 10a+ and 10b+.

Burrell and Officier reported synthesis, structure and properties of bis(ferrocenyl)porphyrins, the $\alpha$-$\alpha$-5,15-bis(ferrocenyl)-2,8,12,18-tetraphenyl-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 $K_c$ calculated from the separation of the voltammetric waves, $1.6 \times 10^3$ for 11 and $8.5 \times 10^2$ 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 $\Delta\tilde{\nu}_{1/2} = 1400$ cm$^{-1}$ for Ni-11+ with the value calculated by mean of eq. 5 (4900 cm$^{-1}$) indicates that this cation is a class III (highly delocalized) mixed-valence species. For 11+, the experimental value $\Delta\tilde{\nu}_{1/2} = 2600$ 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 R,R-5,15-bis(ferroceny)-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrin.

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-tolylioporphyrin 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 ($C_{5v}$) 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 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.
While CV experiment of 12 in the coordinating acetonitrile, using the traditional nBuNPF₆ as 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 nBuNB(C₆F₅)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 nBuNB(C₆F₅)₄ was mainly attributed to the presence of significant electrostatic repulsion between the two non-ion-pairing cationic centres in the diocation. 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 π system of the porphyrin is an efficient platform for electron transfer between ferrocenyl, Nemykin and Galloni prepared and characterized the “trans” 5,15-bis(ferrocenyl)-10,20-diphenyl (14) and the “cis” 5,10-bis(ferrocenyl)-15,20-diphenyl (15).

The electrochemical removal of individual electrons from the ferrocene substituents indicated the existence of long-distance metal-metallation interaction in both cis and trans isomers, a result supported by spectruelectrochemical and chemical oxidation experiments. Within CV experiments, the first oxidation of trans 14 occurred at lower potential then that of cis 15 and the ΔE separation between the two ferrocenyl-based oxidation wave 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⁺ (v_max = 11700, 11000 cm⁻¹, ε_max = 9300, 6100 M⁻¹ cm⁻¹ and Δv_r,2 = 2900, 4100 mV, respectively). The related comproportionation constants are large enough to form stable mixed-valence species.

However, when the electronic coupling is pronounced, the true electron transfer distance r can be considerably shorter than the geometric distance r₂. Indeed, we note that the narrowness of the bands highlighted by comparing the experimental and calculated (eq. 8) half-bandwidths Δv_r,2 was more pronounced for the trans 14⁺. The value of the parameter 1/ε′ (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-dithiolenyl)]ferrocenyl]-15,20-di-p-tolylporphyrin and trans 5,15-bis[1-(2,1,3-dithiolenyl)]ferrocenyl]-10,20-bi-p-tolylporphyrin, although based only on the value of the volumetric ΔE splitting.

In a series of papers recently reviewed by the same author, 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 ΔG_e = −FΔνE given by the statistical distribution (RT/F)ln(1/4), the electrostatic interaction (ΔG_s), the inductive factor (ΔG_i), and the resonance stabilization (ΔG_r).

A family of bis(ferroceny) five-membered heterocycles (16–24) were prepared and analysed.

Electrochemical CV and SWV measurements were carried out in dichloromethane in the presence of nBuNBPF₆ or nBuNB(C₆F₅)₄ as the supporting electrolyte. The use of dichloromethane and nBuNB(C₆F₅)₄ resulted in a better resolution due to the lower ion-pairing capabilities of B(C₆F₅)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 monocatenic molecules. The enlargement of the wave separation is similar along the series 16–19 (130–140 mV). 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 revealed similar trends of the electrochemical properties, with the more easily oxidized complexes bearing the more electron donating heteroatoms, giving rise to larger ΔE values and accordingly higher stability of corresponding mixed-valence cations, in the sequence NPh (450 mV) ≫ NMe (410 mV) > O (290 mV) ≈ R (280 mV) > S (260 mV).

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

$$\text{const} = RT \ln 1/4 + \Delta G_e + \Delta G_{\text{in}} \quad (16)$$

For the cations 16⁺–24⁺, the oscillator strength f₁₄, 16 of the IVCT absorptions increases with the degree of intermetallic communication:

$$f = (4.6 \times 10^{-6}) e_{\text{max}}^2 \Delta v_{r,2} \quad (17)$$

The cations 16⁺–24⁺ showed a linear relationship between ΔE 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 ΔE (Fig. 3). From the slope, the effective electron transfer distance r was calculated (2.05 ± 0.05 Å), much shorter than the geometrical iron–iron distances, and used to determine r parameters according to Hush equation (eq. 6).
\[
\frac{f}{4.6 \times 10^{-3}} = \frac{\text{const} \times r^2}{8.49 \times 10^{-4}} + \frac{F \times r^2}{8.49 \times 10^{-4}} \Delta E \quad (18)
\]

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

Barlow and O’Hare\(^{46}\) synthesized a series of mixed bis(ferrocenyl) complexes in which two FeCp\(^*\)Cp \((\text{Cp}^* = \text{pentamethylcyclopentadieny})\) are linked by the saturated bridges CMe\(_2\), SiMe\(_2\), GeMe\(_2\) and SiMe\(_4\). SWV of order CMe\(_2\) > SiMe\(_2\) > GeMe\(_2\), a result consistent with the increasing between the oxidation waves decreases for the bridging ligand in the order CMe\(_2\) > SiMe\(_2\) > GeMe\(_2\). This observation is unusual if compared with previous results on metallocenes linked by saturated bridges. In a Class II mixed-valence species, the max were classified as Class II mixed-valence species. In a Class II system, the \( \tilde{\nu}_{\text{max}} \) energy of the IVCT band represents the reorganisation energy \( \lambda \) for the intramolecular electron-transfer reaction. The value of \( \tilde{\nu}_{\text{max}} \) 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 metallocones linked by saturated bridges. In those studies, a stronger coupling through a Si-bridge was suggested,\(^{10b, 47}\) due to conjugation through empty, low-lying \( \sigma^* \) or \( \delta \) orbitals of Si, which may enable greater coupling.\(^{48}\)

Differently, Barlow and O’Hare suggested that the decrease in the order CMe\(_2\) > SiMe\(_2\) > GeMe\(_2\) indicates that the coupling is predominantly through space in 25\(^{-}–27\). 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) containing two terminal ferrocenyl units and based on the strongly foldameric \( \alpha \)-aminoisobutyric (Aib).\(^{49}\)

The electronic coupling was quantitatively probed by the analysis of the IVCT absorption in the NIR region of mixed-valence cation. 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 \( \tilde{\nu}_{\text{max}} \) energy of the IVCT band represents the reorganisation energy \( \lambda \) for the intramolecular electron-transfer reaction. The value of \( \tilde{\nu}_{\text{max}} \) 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 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 electron 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 mononuclear ferrocenyl-peptides,\(^{50}\) depend on the position of the ferrocenyl groups in the chain and on macrodipole orientation (Fig. 4).

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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 Fc 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.51

Metal-metal electron delocalization in linkage structures assembled via noncovalent are extremely rare. Kaifer52 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 centres 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 IVCT band in the NIR spectral region at \( \tilde{\nu}_{\text{ex}} = 8370 \text{ cm}^{-1} \). Surprisingly, the spectral characteristics, in particular the experimental bandwidth (\( \Delta \tilde{\nu}_{\text{ex}} = 560 \text{ cm}^{-1} \)) compared to the value predicted by Hush theory (eq. 6, \( \Delta \tilde{\nu}_{\text{ex}} = 4400 \text{ cm}^{-1} \)), 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 ferrocene moieties, 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,53 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 joins the family of molecular electronics54 in the QCA paradigm and found a successful application with 3,6-bis(1-ethylferrocen)-9H-carbazol-9-y1-6-hexan-1-thiol (35) and its enantiomers.55

In a QCA, the interplay between electronic coupling and electrostatic interaction is a crucial point: quantum dots are arranged in functional cells connected by tunneling 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. 5). The adjacent cells interact electrostatically and their ground state configuration depends on the reciprocal charge positioning in the cells. In fig. 5, 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.56

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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 were obtained at low temperature (218 K) and lower scan rate (1 V s⁻¹).

At more positive potentials the reversible two-electron oxidation peak \( E_{1/2} = 1.25 \text{ V} \) 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-diethiols 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

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*Dalton Trans.*, 2014, **00**, 1-3 | 9
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 correct QCA operation.

**Tris(ferrocenyl) complexes**

Investigations on three families of tris(ferrocenyl) systems⁵⁷, 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 simple bimetallic molecules and that in multi-component systems.

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)⁵⁹ and Si (43)⁶⁰ were also synthesized.

![Diagram of tris(ferrocenyl) complexes](image)

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)phosphate 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.⁵⁹

Monoxidized tris(ferrocenyl)borane (36) and tris(ferrocenyl)phosphine (38) did not exhibit the NIR transition. The IVCT band found for the σ-bond bridged derivative 42 was attributed to a through-space mechanism. Conversely, it was suggested that the presence of the transition in the phosphate oxide 41, absent in the phosphine derivative, may be due to a difference in the dp-π overlap of phosphorus and the cyclopentadienyl rings in the two systems.⁶⁰

Tris(ferrocenyl)amine (37) showed three well-resolved reversible oxidation waves within CV experiments in acetonitrile with NaClO₄.⁶¹ This is an unusual molecule, as shown by its molecular structure,⁶² since it contains three ferrocenyl groups surrounding an almost planar nitrogen atom. In addition, the short C(=O)-N bonds (average 1.414 Å) indicate partial double-bond character between the nitrogen and the cyclopentadienyl ring suggesting the existence of a strong electronic interaction between the amine nitrogen and the ferrocenyl substituents, resulting in resonance interaction as an important factor in the stabilization of the ferrocenium by nitrogen.

CV of trifunctional silane (43) displayed three reversible oxidation waves in dichloromethane solutions containing either PF₆⁻ or Bi(C₆F₅)₃⁻ electrolyte anions, closely spaced with nBu₄NPF₆ and well-separated with nBu₄NB(C₆F₅)₄, indicating a good interaction between the ferrocenium moieties.⁶⁰ Applying to these results what suggested by Astruc,⁵⁹ when nBu₄NPF₆ is used as the supporting electrolyte in dichloromethane, the strong ion pairing between PF₆⁻ and the cationic substrates leaves very little electrostatic effect. The observed splitting between the subsequent CV waves of the equivalent ferrocenyl groups should roughly correspond to electronic interaction in the absence of other significant factors, possibly with a through-space mechanism. The increased wave separation in the presence of nBu₄NB(C₆F₅)₄ is reasonably due to electrostatic interaction.

Recently, Lang⁶³ presented the synthesis, electrochemical and spectrototroelectrochemical behaviour, and DFT calculations of “star-shaped” tris(ferrocenyl) substituted six-membered (hetero)aromatic benzene (44), pyridine (45), and triazine (46).

![Diagram of tris(ferrocenyl) complexes](image)

In contrast to the electrochemical investigation of 44 using nBu₄NCIO₄ as supporting electrolyte in benzonitrile, resulting in a simultaneous oxidation of the three ferrocenyl substituents,³¹ the use of nBu₄NB(C₆F₅)₄ allowed the separation of the redox events. Similarly, the tris(ferrocenyl)-substituted molecules 45 and 46 showed three well-defined and separated reversible one-electron redox processes. According to the ΔE values, the thermodynamic stability of the mixed-valence species, determined by the disproportionation constant $K_c$, increased in the order 46 > 45 > 44. Concerning the nonresonance terms of ΔG_c, the increase of ΔE splitting and $K_c$ was attributed to the stabilization of the charge by delocalization into the aromatic ligand.

For the mixed-valence species 4⁴⁺ and 4⁵⁺ ($n = 1, 2$) broad and low-energy absorptions between 10000 and 4000 cm⁻¹ with different intensities were observed. These IVCT transitions are indicative of electronic interactions between the Fe(II)Fe(III) iron centres along the benzene and pyridine bridges. Their spectroscopic characteristics allowed assigning the mixed-valence to very weak coupled class II systems. Interestingly, the absence of ΔE splitting for 44 with nBu₄NCIO₄ as supporting electrolyte was not symptomatic of lack of electronic coupling.

No absorption in the NIR region appeared by oxidation of 46, allowing the classification of this compound as a class I system. Thus, the observed ΔE splitting was attributed to electrostatic interactions between the positively charged ferrocenyl groups in 3⁵⁻ and 4⁶⁻, and the highest ΔE values found for 46 were ascribed to the nonresonance terms of ΔG_c.

These results prompt to conclude that systems with similar architecture and splitting between consecutive redox waves may still differ with respect to the nature and strength of the electronic interactions.

The CV of “star-shaped” 1,3,5-tris(ferrocenyl)ethynylenzene complex 47 reported by Astruc 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 nBu₄NB(C₆F₅)₄.

However, for meta-bis(ferrocenyl)ethynylenzene (6m) as well as for the 1,3-bis(ferrocenyl)ethynylenzene complexes containing bromo (48), ethynyl (49), trimethylsilyethyl (50) and pentamethylferrocenylethynyl (51) substituents in the third meta
position, only a single wave was observed for the two ferrocenyl
group even with \( n\text{Bu}_4\text{NB}(\text{C}_6\text{F}_5)_4 \).

In these compounds, in order to minimize the electrostatic repulsion,
the two oxidized ferrocenyl groups were supposed to lie at opposite
sides 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 lie at an intermediate position
enhancing the electrostatic effect among the three positively charged
sites and causing the splitting of the three ferrocenyl CV waves. 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
of dihydro-1H-trindene (TdH), a polycyclic hydrocarbon
synthesized by Katz and Ślusarek in the early 1980s. The use of
TdH as a metal bridging ligand is particularly favourable becaus
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. 6), 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 \( \text{nBu}_4\text{NP}F_6 \) to
\( \text{nBu}_4\text{NB}(\text{C}_6\text{F}_5)_4 \).

As a result of the \( \Delta E \) splitting, 53\(^+\) and 54\(^+\) can be selectively
produced in solution.

![Fig. 6 Oxidative CVs in dichloromethane, scan rate \( \nu = 0.5 \text{ V s}^{-1} \), of 53 with
(a) 0.1 M \( \text{nBu}_4\text{NP}F_6 \), (b) 0.1 M \( \text{nBu}_4\text{NB}(\text{C}_6\text{F}_5)_4 \), (c) SWV with 0.1 M
\( \text{nBu}_4\text{NB}(\text{C}_6\text{F}_5)_4 \). Oxidative CVs in dichloromethane of 54 with (d) 0.1 M
\( \text{nBu}_4\text{NP}F_6 \), (e) 0.1 M \( \text{nBu}_4\text{NB}(\text{C}_6\text{F}_5)_4 \), (f) SWV with 0.1 M \( \text{nBu}_4\text{NB}(\text{C}_6\text{F}_5)_4 \).

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 nucleophilic supporting electrolytes was
not indicative of lack of electronic coupling.

Pertaining to linear multi(ferrocenyl) systems, in one of its ear
works Meyer\(^{67}\) 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 > 56 > 55. Weakly electronic coupling was measured between Fe(II) and Fe(III) sites for the mixed-valence ions of 55+55− and 56+.

In particular, the IVCT energy of the mixed-valence cation 55+ detected in the NIR region ( \( \bar{\nu}_{\text{max}} = 5590 \text{ cm}^{-1}, \varepsilon_{\text{max}} = 1720 \text{ M}^{-1} \text{ cm}^{-1} \)) was similar to that found for (Fc−Fc) ( \( \bar{\nu}_{\text{max}} = 5260 \text{ cm}^{-1}, \varepsilon_{\text{max}} = 760 \text{ M}^{-1} \text{ cm}^{-1} \)), supporting valence localization (Class II) for the trinuclear system. The presence of two donor FeIII centres and one acceptor FeII centre is responsible of the intensity enhancement of a factor of two in the IVCT band of 55+ over the (Fc−Fc+) case.

Even if the central ferrocenyl unit is reasonably the first centre to be oxidized, as it bears two electron-donating substituents, reactants and products of electron transfer in 55+ are almost energetically equivalent, being the energy difference between (Fc−Fc−Fc) and (Fc−Fc−Fc−Fc) with the former slightly favoured by the ferrocenyl substituent effects ( \( \approx 30 \text{ mV} \)) and the latter by a statistical factor of 2 ( \( \approx 18 \text{ mV} \)). The IVCT molar absorption coefficient of 55+ was much higher than that of (Fc−Fc)+. This enhancement, typical of these 1,1’-oligoferroocene, was explained by considering the existence for 55+ of two equivalent transitions, that are Fe−Fc−Fc−Fc→Fc−Fc−Fc→Fc−Fc−Fc−Fc→Fc−Fc−Fc−Fc−Fc→Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fc−Fs...
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{72} and 71\textsuperscript{72,75} were not reported.

We have recently reported the synthesis of the prototypical cyclic
metallocene triads, namely the isomers syn,syn,anti-[FeCp]\textsubscript{3}Td
(72) and syn,syn,syn-[FeCp]\textsubscript{3}Td (73) which can be figured out as the “fusion” of three ferrocenes into a rigid cyclic array.\textsuperscript{73}

The CV oxidation of 72 in dichloromethane/nBu\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 (\(E_0 = 0.94\) V) with a typical stripping peak as its cathodic counterpart (Fig. 7).

The \(\Delta E\) 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{2+} which could be
generated by chemical oxidation and analysed at room temperature by optical spectroscopy.

![Fig. 7 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\(^{-1}\), \(T = 20\) °C.](image)

Gaussian deconvolution of the spectrum obtained in the NIR/IR region showed three IVCT bands at 3430, 5310 and 7030 cm\(^{-1}\) (Fig. 8).

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{106} due to the possibility of itinerant “extra” electron hopping over the coupled sites.\textsuperscript{74}

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{12a,b} although this effect were
not been experimentally verified before.\textsuperscript{106}

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{75}

The IVCT bands of 72\textsuperscript{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{75}

![Fig. 8 NIR/IR spectrum of the 72\textsuperscript{2+} cation in dichloromethane (straight line) and Gaussian de-convolution (dashed lines).](image)

The \(I\) value (0.51–0.55 from eq. 9) obtained for the three bands
supported the assignment of the mixed-valence 72\textsuperscript{2+} to the borderline
Class II–III.

These results suggested that introduction of the third fused
ferrocenes favours the localized-to-delocalized transition and are
consistent with fast electron transfer and valence averaging on the
NIR/IR timescale with no contribution of the solvent to the
reorganization energy. As expected for a Class II–III regime, the
solvent is averaged and the spin density, according to DFT
calculations on 72\textsuperscript{2+}, is localized.

The spectrum of 73\textsuperscript{3+} revealed a well-defined band at higher energy
(10480 cm\(^{-1}\)) and lower intensity than that of isomer 72\textsuperscript{2+}. The value of \(I = 0.31\) were indicative of a weaker metal–metal electronic
coupling when the three iron are in a syn,syn,syn configuration, but higher
that that found for the structurally related bimetallic cation
75\textsuperscript{3+}.

**Tetra(ferrocenyl) complexes**

Homoleptic tetra(ferrocenyl), EF\textsubscript{4}, derivatives of the Group 14
elements C, Si, Ge, Sn, and Pb have been prepared (76–80).\textsuperscript{58}
SiF\textsubscript{4} \textsuperscript{77,76} and Sn[(C\textsubscript{6}H\textsubscript{5})\textsubscript{2}(C\textsubscript{5}H\textsubscript{5}CH\textsubscript{2}NMe\textsubscript{2})Fe]\textsubscript{4} \textsuperscript{82} 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.

![Diagram of Fe₄ compounds](image)

Remarkably, oxidations with an even larger overall spread of 590 mV. The intensity of which increased up to 2–3 equivalents of oxidant added, EFc₄ compounds indicated that electronic communication occurs with a splitting of 0.12 V each, suggesting some interaction. The lack of coplanarity of the redox-active subunits in the congested was oxidized in three steps to the tetracation in a 1e/1e/2e sequence. The spread of the four potentials over 420 mV indicated appreciable interactions among the ferroceny1 groups upon successively oxidation. Instead, a solution of 82 in dichloromethane/nBu4NPF6 was oxidized in three steps with splitting of 0.12 and 0.14 V in a 2e/1e/1e sequence.

The zwitterion BFc₄ has been characterized as a mixed-valence system in solution with a broad IVCT band at 4550 cm⁻¹ and localized valencies in the solid state. The cations 84⁺ and 84₂⁺ were isolated and characterized. In particular, electrochemistry of 84 and NIR spectra of 84⁺ and 84₂⁺ have been re-examined in a 1:1 mixture of CH₃CN. 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/C). The bands observed for 84⁺ and 84₂⁺ were assigned to IVCT transitions, that of 84⁺ occurring at higher energy. The solvent dependence of ∆λ₁max 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⁺ and two Fe° sites were observed in both the IR and Mössbauer spectra of 84⁺ and 84₂⁺, indicating that these cations are valence trapped, class II, compounds on the 10⁻¹² s IR time scale.

The valence trapping observed in the solid state suggests that 84⁺ 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. The tetra(ferrocenyl) substituted porphyrin (85) has been prepared and investigated by Nemkin and Galloni, and is undoubtedly a potential candidate for application in QCA device, and a photoactive material for photoelectrochemical cells. The electrochemical properties of 85 were studied using CV, DPV and SWV methods in different combinations of solvent and supporting electrolyte.

Heinze has isolated and fully characterized the substituted tetraferrocenylstannane Sn[(C₅H₄COOCH₃)(C₅H₄)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 electronic communication occurs through-space 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 Kc.

Stepwise oxidation of 83 with AgSbF₆ in dichloromethane showed the appearance of an absorption band around 5000 cm⁻¹, the intensity of which increased up to 2–3 equivalents of oxidant added, indicating the formation of 83⁺² via 83⁺ and assigned to IVCT transitions. The electronic coupling H in 83⁺ and 83⁺² (145 and 220 cm⁻¹, respectively) was estimated using the Hush relationship (eq. 6) with r = 6Å (∆λ₁max = 4800, 4500 cm⁻¹, ε₁max = 125, 280 M⁻¹ cm⁻¹ and ∆λ₁max = 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 weakly coordinating $n\text{BuNB}(\text{CaF}^+)_3$ 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 $0.34 \text{ V vs Fe/Fe}^+$ in which 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 $n\text{BuNPF}_6$ electrolyte ($E_{1/2} = -0.01, 0.08, 0.14$ and $0.25 \text{ V vs Fe/Fe}^+$).

The increased wave separations, observed when the weakly coordinating anion $\text{BF}_4^-$ 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 $85^{2+}$. On the other hand, the persistence of a $\Delta E$ splitting in traditional electrolyte containing the anions $\text{BF}_4^-$ or $\text{PF}_6^-$, which may react as nucleophiles with radical cations, corresponds approximately to the electronic communication in the absence of other significant factor.\(^{29a}\)

Two processes are conceivable for the formation of $85^{2+}$, 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 $85^{2+}$ and $85^{3+}$ mixed-valence species as well as of $85^{4+}$. The IVCT bands observed in the NIR region for $85^{+}$, $85^{2+}$ and $85^{3+}$ 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 $85^{2+}$ and $85^{3+}$ was also confirmed by MIR, Mössbauer and XPS data.

These remarkable properties prompted Galloni and Niemynk’s groups to prepare and characterize novel tetra(ferrocenyl)porphyrin containing self-assembled monolayers (SAMs), and a preliminary investigation on their photocurrent generation efficiency.\(^{35}\)

The electrochemical and optical properties of tetra(ferrocenyl) substituted thiophene, furan and pyrrole $86$–$89$ were prepared and investigated by CV, SWV and in situ UV–vis/NIR spectroscopy by Lang.\(^{42b–c}\)

As the iron–iron distances in this series are almost equal, the electrostatic contribution to the $\Delta E$ separation were 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 high 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 $86^+$, 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 $86^+$–$89^+\ (eq. 17 and 18$) and allowed to estimate the electron transfer distance $r$, as for the series bis(ferrocenyl) heterocycles $16^+$–$24^+$. The electronic coupling in tetraferrocenyl heterocycles $86^+$–$88^+$ 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 group with the central heterocycles due to the higher steric demand in the more crowded $86^+$–$88^+$ series.

Electrochemical and optical investigations on linear tetra(ferrocenyl) systems were reported by Meyer\(^{57}\) (56), Nishihara\(^{48}\) (59) and Geiger\(^{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 of 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 these the penta(ferrocenyl) derivatives $90$–$92$.\(^{85}\)
The lack of coplanarity of the central cyclopentadienyl, evidenced by X-ray structure, attenuates but does not remove intermetallic interaction in 90, as indicated by CV data in CH₂Cl₂ / nBuNPF₆, which displayed three oxidation waves at E₁/₂ = 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 sp²-carbon is oriented out of the mean plane of the cyclopentadiene. Comparison of the CV data (E₁/₂ = −0.11, 0.17 and 0.33 V) with that of 90, revealed clearly the effect of isolating electronically the sp³-bonded ferrocenyl from the rest of the molecule.

The anion 92 showed three oxidation steps at E₁/₂ = −1.25, 0.20, and 1.20 V, reflecting the transitions from anion → radical → cation (possibly ferrocenyl centred) → dication.

Similarly to what observed in the very crowded EFc₄ complexes, we believe that the metal–metal interaction is essentially due to electrostatic effect. Unfortunately, neither the effect of the weakly coordinating nBu₄NB(C₆F₅)₄ on the wave multiplicity and separation, or the presence of mixed-valence cations were verified.

The advances in manipulation of single molecules⁸⁶ have stimulated much interest in the synthesis of molecular machines,⁸⁷ as nanowheels,⁸⁸ nanocars,⁸⁹ and nanogears.⁹⁰

The possibility to observe and exploit a controlled rotation on a surface was also verified.⁹²

Hexa(ferrocenyl) complexes

Electrochemical and optical investigations on linear hexa(ferrocenyl) systems were reported by Nishihara⁷⁸ (59) and Geiger⁷⁹ (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 hexaferrocenylbenzene (94).⁹³

The CV in CH₂Cl₂ / nBuNPF₆ exhibited well separated redox waves at E₁/₂ = −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 nBu₄NB(C₆F₅)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.⁹⁷

The CVs of 95–97 in CH₂Cl₂ showed a single wave when nBuNPF₆ was used as the supporting electrolyte, as well the CVs of the structurally related bis(ferrocenyl) 6p and tris(ferrocenyl) 47 complexes.

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 CH₂Cl₂ containing nBuNPF₆, 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. Electronic coupling is here an undesirable phenomenon since it would allow intramolecular charge transfer between neighbouring ferrocene centres, without actual turning of the rotor; (iii) the rotation barrier of the rotor was very low, as shown by NMR and DFT calculations.
The lack of wave splitting $\Delta E$ was attributed to the absence of significant intramolecular communication between the iron ions. The CVs were also recorded with $n$Bu$_4$NB(C$_6$F$_5$)$_4$ 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 B(C$_6$F$_5$)$_4^-$ 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 ortho, meta, and para positions (Figure 9).

![Fig. 9 Oxidation mechanism of 95 in the presence of $n$Bu$_4$NB(C$_6$F$_5$)$_4$ in CH$_2$Cl$_2$.](image)

The CV of 96 with $n$Bu$_4$NB(C$_6$F$_5$)$_4$ 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.

The hexa(3'-ferrocenylphenyl)benzene (98) was prepared by Chebnya$^{94}$ The CV of 98 in CH$_2$Cl$_2$ and $n$Bu$_4$NP$_6$ 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 98$^{9+}$ which showed a band in the NIR region ($\nu_{\text{ex}} = 9050$ cm$^{-1}$, $\varepsilon_{\text{ex}} = 1400$ M$^{-1}$ 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',4',4',5',5'-hexaferrocenyl-2,2'-bithiophene (99) and the related 3,4,5-tris(ferrocenyl)thiophene (100), recently prepared by Lang.$^{42a,95}$

![Fig. 9 Oxidation mechanism of 95 in the presence of $n$Bu$_4$NB(C$_6$F$_5$)$_4$ in CH$_2$Cl$_2$.](image)

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/Fe$^+$ were observed for the trinuclear 100 in dichloromethane solutions using $n$Bu$_4$NB(C$_6$F$_5$)$_4$ as supporting electrolyte. The hexanuclear 99 displayed five redox processes at $E_{1/2} = -0.165, 0.26, 0.49, 0.65$ and 0.80 V vs Fe/Fe$^+$ in anisole/$n$Bu$_4$NB(C$_6$F$_5$)$_4$, the first one corresponded to two one-electron events close together, followed by four separated one-electron waves. Stepwise oxidation of the ferrocenyl groups was obtained by spectroelectrochemistry. Surprisingly, while mono-oxidated 100$^+$ and 100$^{2+}$ 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 99$^{n+}$ (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 $K_e$ 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 $\text{B(C}_6\text{F}_5)_4^-$, 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


