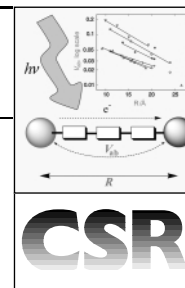


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Long-distance intervalence electron transfer can be monitored by the quantitative study of intervalence transitions in series of binuclear mixed-valence metal complexes, with metal–metal distances reaching 25 Å. This allows the determination of the electronic coupling  $V_{ab}$ , and its rate of decay with distance. Comparisons are made between several series of compounds, and also with organic mixed-valence systems. The decay is exponential with a coefficient varying in a relatively narrow range (0.08 to 0.12 Å<sup>-1</sup>). Applications for molecular switching are discussed.

## 1 Introduction

Intervalence electron transfer occurs in mixed-valence compounds, *i.e.* compounds made of two or more redox sites existing in different oxidation states. These compounds are thus particularly convenient for the fundamental study of the ubiquitous process of electron transfer. The present review is mainly devoted to symmetrical mixed-valence complexes, in which two metal atoms are connected by a bridging ligand, with the general topology shown in Fig. 1. Several reviews have already appeared on such compounds,<sup>1–3</sup> but we shall concentrate here on recent results in the field. A few examples of organic mixed-valence systems will also be discussed. In most cases of inorganic complexes, the metal atoms are in fact end groups necessary to define a starting site and an arrival site, while the spacer is usually purely organic. It plays the role of a molecular wire, *i.e.* it makes possible the electron transfer

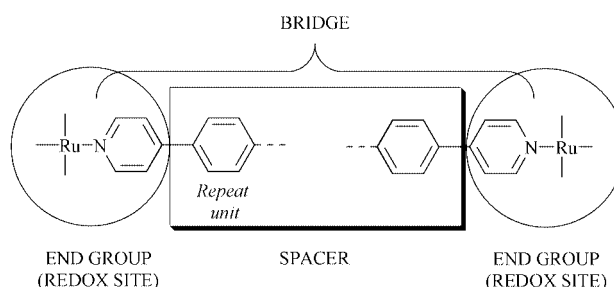


Fig. 1 General structure of mixed-valence compounds, with definitions of end group (redox site), bridging ligand, spacer and repeat unit.

between these two sites, more efficiently than if they were separated by empty space.

The distinction between the end groups and the spacer (the wire itself) is not a trivial one. It seemed logical to us to incorporate in the definition of the end groups the immediate coordination sphere: for instance, the coordinated pyridine ring in complexes of the Creutz–Taube family.<sup>1</sup> Thus, the spacer would form the rest of the structure, even if it has no independent chemical existence. In a number of cases, the spacer is made of several *repeat units*, in order to allow the construction of long molecules by repetitive synthesis or even polymerization. Finally, one has to distinguish the *spacer* from the *bridge*, the latter including the coordination sites. The definition of all these terms is made clear in Fig. 1.

Among the numerous bimetallic complexes known in the literature, we have selected those for which the metal–metal distance exceeds a minimum value, taken as 10 Å. The metal–metal distance provides an easy way to compare structures, and the 10 Å limit selects complexes for which relatively uncommon processes may occur. Note that with the above definition, complexes with the ligand 4,4'-bipyridine (M–M distance 11.3 Å) contain only the end groups, but not, strictly speaking, a spacer.

The study of intervalence transitions offers distinct advantages over other methods of studying electron transfer: (i) it is based on simple static spectroscopic measurements, (ii) there is no intervention of thermodynamic factors, because the thermal reactions occur at or near  $\Delta G^\circ = 0$ , and (iii) there is a simple relation with a basic parameter, the electronic coupling term  $V_{ab}$ .

The present review will treat in detail the important problem of *distance dependence* of electron transfer, because it has strong implications in various domains of chemistry, biology, physics, nanosciences, *etc.* In chemistry, a major challenge is the realization of a molecular switch (see Section 5), which necessitates the mastering of long-distance electron transfer (over 15–20 Å), because a switching unit must be inserted on the electron transfer path. In biology, it is important to know how electrons can move in redox proteins such as cytochromes across essentially non-conjugated parts, or how a chemical signal can be converted in an electrical one for making biosensors. In physics and nanosciences, the knowledge of intramolecular electron transfer is useful to devise (bulk metal)–

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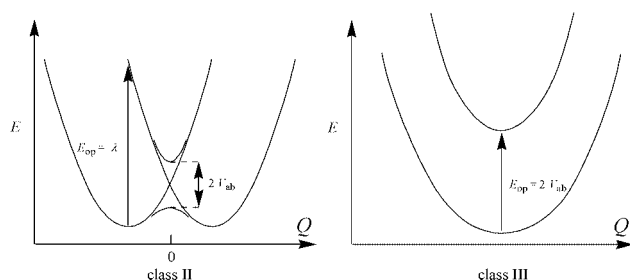


single molecule–(bulk metal) nanojunctions. Current research in the area is also devoted to the problem of electron transport by the tunnel effect across the molecule, and its distance dependence.

## 2 Intervalence transitions and electronic coupling

### 2.1 Mixed-valence compounds and their potential energy curves

Electron transfer reactions are currently described by potential energy curves of the Marcus type (see Fig. 2). Basically, the



**Fig. 2** Potential energy curves for class II and class III mixed-valence compounds.  $\lambda$  is the reorganization parameter and  $V_{ab}$  the electronic coupling.  $E_{op}$  is the energy of the intervalence transition.

potential energy of the complete system is plotted as a function of a reaction coordinate  $Q$  defining the changes in both the inner and outer coordination spheres.<sup>1,3</sup> For zero order, two such curves can be constructed, corresponding to the two limiting electronic structures Red–Ox and Ox–Red, where Red and Ox designate the reduced and oxidized state of a site. The  $\lambda$  parameter is linked to the reorganisation energy of a site when it is oxidised or reduced. In the absence of electronic interaction, the curves are parabolas displaced laterally with respect to each other. However, the electronic interaction modifies this simple picture by allowing a mixing of the wave functions and a change in the energies. It is described by an electronic parameter  $V_{ab}$ , also called “tunneling matrix element”, “resonance exchange integral”, or “coupling element”, which is responsible for avoided crossing between the two zero-order parabolas.

Note that the diagram (Fig. 2) is initially formulated in terms of potential energy, but a detailed analysis through statistical thermodynamics shows that a representation in terms of free enthalpy changes is valid<sup>4</sup> (although pedagogically not recommended!).

According to the relative values of  $\lambda$  and of the electronic coupling  $V_{ab}$ , two situations may occur: small or large electronic coupling. If the electronic coupling is small (and/or if  $\lambda$  is great) the lowest potential energy surface still possesses two minima, and two different electronic states can exist (Fig. 2, left). They can interconvert by a thermal process, the rate of which depends on the height of the energy barrier. In the strong coupling case, the activation barrier has disappeared, and there is a single, completely symmetrical, electronic and nuclear state (Fig. 2, right). This distinction corresponds to the earlier classification of Robin and Day, *i.e.* class II (partly localized) *vs.* class III (completely delocalized) cases.<sup>5</sup>

The determination of the nature (class II *vs.* class III) of a mixed-valence compound is not straightforward, because the observed behaviour depends on the time scale of the electron transfer process with respect to the time scale of the experimental technique. Reliable conclusions necessitate the conjunction of several experimental methods with widely different time scales. But now, due to the progress of theoretical methods, it is possible to assess this problem through computation.<sup>6</sup>

Here we concentrate on weakly coupled systems (class II), but a few examples of class III compounds will be discussed.

We shall consider more specifically chemically symmetrical systems for which the two minima are of equal height.

As shown by Hush,<sup>7</sup> in a class II system, there are two kinds of intramolecular electron transfer: a thermal one, and an optical one corresponding to the so-called intervalence transition (Fig. 2). In the limit of zero electronic interaction, the thermal activation energy is just  $\frac{1}{4}$  of the optical energy, due to the parabolic nature of the curves. From an experimental point of view, the role of  $V_{ab}$  is twofold: (i) it allows the system to jump from one zero-order parabola to the other when arriving in the avoided crossing region, which corresponds to the thermal electron transfer process, the rate of which is proportional to  $(V_{ab})^2$ ; (ii) it mixes the electronic wave function of the ground state with that of the excited state, which determines the intensity of the intervalence transition, also proportional to  $(V_{ab})^2$ . Thus,  $V_{ab}$  is one of the key parameter determining the system's behaviour.

The other important parameter, the reorganization term  $\lambda$ , is usually broken down in two contributions, one  $\lambda_{in}$  corresponding to the bond length changes in the inner coordination sphere (metal–ligand bonds), and the other  $\lambda_{out}$  corresponding to changes in the solvation state.<sup>1,3</sup> The most common formula for  $\lambda_{in}$  is, in the case of a metal<sup>II</sup>–metal<sup>III</sup> mixed-valence system given by eqn. (1), where  $n$  is the number of bonds subject to change (*i.e.* 6 for octahedral redox sites),  $k_{II}$  and  $k_{III}$  are the force constants for oxidation states II and III, and  $d_{II}$  and  $d_{III}$  are the equilibrium distances for the metal–ligand bonds. For  $\lambda_{out}$ , eqn. (2) holds where  $\Delta e$  is the amount of charge transferred ( $= 1e$  for an optical intervalence transfer),  $a_A$  and  $a_B$  are the radii of the two redox sites,  $R$  is the metal–metal distance, and  $\epsilon_s$  and  $\epsilon_{op}$  are the static and optical relative permittivities, respectively.

$$\lambda_{in} = n \frac{k_{II} + k_{III}}{2} (d_{II} - d_{III})^2 \quad (1)$$

$$\lambda_{out} = \frac{\Delta e^2}{4\pi\epsilon_0} \left( \frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \left( \frac{1}{2a_A} + \frac{1}{2a_B} - \frac{1}{R} \right) \quad (2)$$

For a class II system, the energy of the intervalence transition is given by  $\lambda$ , even when the degree of ground state delocalization is high, *i.e.* near the border with class III systems. Usually, the corresponding transition occurs in the near-IR region, typically between 1000 and 2500 nm, where generally few electronic transitions are present. However, as will be seen below, efficient systems are those that also undergo low energy charge transfer transitions, either metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT), which can more or less overlap with the intervalence band. Thus, it is advantageous to deal with intervalence bands occurring at the highest possible wavelength. Eqn. (1) shows that the best systems are those for which the geometrical changes between the oxidized and reduced states are minimal. With respect to the solvent contribution, eqn. (2) shows that for long systems, the intervalence band energy will move to higher values (lower wavelength) and may overlap with other transitions.

### 2.2 Intensity of intervalence transitions and electronic coupling

Since  $V_{ab}$  plays a central role in the theory, its determination in the largest possible series of compounds is of great interest. In a two-state model, a simple evaluation of the transition moment, using Mulliken's approach of donor–acceptor systems, yields Hush's equation [eqn. (3), 1967].<sup>7</sup>  $V_{ab}$  is obtained in  $\text{cm}^{-1}$ ,  $\epsilon_{\max}$  is the maximum extinction coefficient for the intervalence transition,  $\bar{\nu}$  is its energy ( $\text{cm}^{-1}$ ),  $\Delta\bar{\nu}_{1/2}$  is its full width at half-maximum, and  $R_{MM}$  is the direct (through space) metal–metal distance. Although more than 30 years old, this equation is still widely used. A recent reinvestigation has shown in particular that its range of validity is wider than previously believed.<sup>8</sup>

Contrary to common belief, it is not only valid for very weakly coupled systems, but also for strongly coupled ones, provided that overlap can be neglected, *i.e.*, for any orthonormal two-state model.

$$V_{ab} = \frac{2.05 \cdot 10^{-2} \sqrt{\bar{v} \Delta \bar{v}_{1/2}} \varepsilon_{\max}}{R_{MM}} \quad (3)$$

A known difficulty in the use of eqn. (3) is the value of the  $R_{MM}$  parameter, which represents an effective distance between localized donor and acceptor charge centroids. It is usually taken as the through-space geometrical distance between sites A and B, but delocalization effects (*i.e.* extensive wavefunction mixing in the ground and excited states), plus polarization effects (*i.e.* changes in electron distribution) can introduce marked differences. This difficulty is discussed in the so-called "Generalized Mulliken-Hush model" (GMH) model.<sup>9</sup> In fact, a more rigorous formulation of eqn. (3) is given by eqn. (4), where  $\mu_{12}$  is the transition moment and  $\Delta\mu_{ab} = \mu_a - \mu_b$  is the diabatic change in dipole moment, *i.e.* the difference between dipole moments corresponding to non-interacting sites. Eqn. (3) is then obtained from eqn. (4) through the approximation (5), with  $R_{MM}$  the trivial through-space distance between the redox sites. But in the frame of the GMH model,  $\Delta\mu_{ab}$  is more correctly given by eqn. (6) where  $\Delta\mu_{12}$  is the difference between the eigenvalues of the adiabatic dipole moment matrix.<sup>9</sup> The advantage of eqn. (6) lies in the fact that  $\Delta\mu_{12}$  and  $\mu_{12}$  can be experimentally evaluated, respectively, from Stark effect measurements,<sup>10</sup> and from the intensity of the intervalence transition. Once  $\Delta\mu_{ab}$  is known from these measurements, using eqn. (5) in reverse allows us to define an effective  $R_{MM}$  distance. Note, however, that this correct procedure has been very scarcely used, due to the paucity of Stark effect experiments.

$$V_{ab} = \mu_{12} \bar{v} / \Delta\mu_{ab} \quad (4)$$

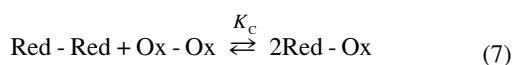
$$\Delta\mu_{ab} = eR_{MM} \quad (5)$$

$$\Delta\mu_{ab} = [(\Delta\mu_{12})^2 + 4(\mu_{12})^2]^{1/2} \quad (6)$$

Finally, for a class III system,  $V_{ab}$  is merely one-half of the optical transition energy (see Fig. 2), and is no longer evaluated from the band intensity.

### 2.3 Experimental determination of $V_{ab}$

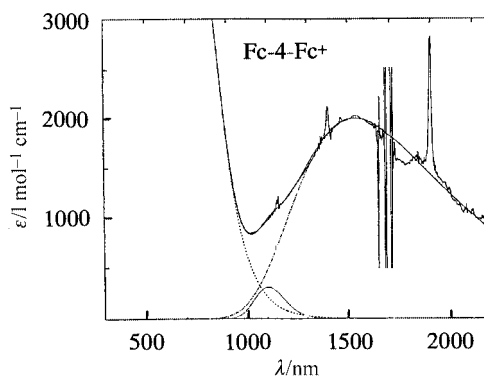
In most of the cases, quantitative intervalence band measurements are performed in solution. Thus, for practical use of eqn. (3), two corrections are generally applied to the experimental spectra. (i) A correction for the comproportionation equilibrium ( $K_c$ ) linking the mixed-valence species with the fully reduced and fully oxidized ones, which is given in eqn. (7).<sup>11</sup> It is easy to show that when the composition of the solution corresponds to the mixed-valence stoichiometry, the proportion  $P$  of complex present in mixed-valence form is given by eqn. (8). The spectrum of the equilibrium mixture can thus be corrected by subtracting the absorptions due to the fully reduced and fully oxidized forms. The  $K_c$  value can be determined either from a redox titration or from the determination of the standard potentials of the Ox–Ox/Red–Ox and Red–Ox/Red–Red couples. This is conveniently achieved by electrochemical methods such as differential pulse voltammetry.<sup>11</sup>



$$P = \frac{\sqrt{K_c}}{2 + \sqrt{K_c}} \quad (8)$$

(ii) A spectral deconvolution. The intervalence band profile is very frequently polluted by the tail of more intense charge

transfer (either metal-to-ligand or ligand-to-metal) transitions. The spectrum must be then decomposed into a sum of gaussian components.<sup>12</sup> An example of an intervalence band profile is given in Fig. 3.



**Fig. 3** Example of an intervalence transition. Spectrum of Fc-4-Fc<sup>+</sup>, *i.e.* a ferrocene and a ferricinium unit linked by four conjugated double bonds, after correction for comproportionation. The decomposition into gaussian components gives the band profile of the intervalence transition, culminating at 1500 nm. (Reprinted from *Inorg. Chem.*, 1996, **35**, 3735,<sup>22</sup> copyright 1996, American Chemical Society.)

Returning now to the comproportionation equilibrium, it is interesting to notice that for large systems ( $R_{MM} \rightarrow \infty$ ) the comproportionation constant tends towards a statistical limit of 4. In this case, a single electrochemical wave is observed, a fact which has frequently dissuaded researchers from further studies on such binuclear complexes. However, even in this apparently unfavourable case, the proportion of mixed-valence species at half-oxidation (reduction) is, according to eqn. (8), a comfortable 50%, allowing nevertheless a meaningful correction. Another method of determining  $V_{ab}$  has been recently described, which does not rely primarily on the intervalence transition. It is based on the Creutz–Newton–Sutin (CNS) model.<sup>3,8</sup> This approach is based on superexchange theory, recognizing that the metal–ligand interactions play a key role in metal–metal interaction, but manifest themselves also as charge transfer transitions (metal-to-ligand or ligand-to-metal). For a class II system, the CNS evaluation of  $V_{ab}$  makes use of eqns. (9)–(11). In eqn. (9)  $H_{ML}$  is the metal–ligand coupling for the Ru<sup>II</sup> site [determined by the intensity and position of the MLCT band by an equation analogous to eqn. (3)],  $H_{ML'}$  is the corresponding quantity for a hypothetical Ru<sup>II</sup> site having the Ru<sup>III</sup> geometry, and  $\Delta E_{ML}$  is the effective energy gap for this transition.  $H_{LM}$ ,  $H_{LM'}$  and  $\Delta E_{LM}$  are the corresponding values for the LMCT transition. Frequently one can neglect the small differences in geometry between the two redox sites, and thus identify terms such as  $H_{ML}$  and  $H_{ML'}$ , giving a simplified version of eqn. (9) in the form of eqn. (10). In most cases, one of the superexchange interactions dominates, and eqn. (10) is further reduced to one term. The effective energy gap is computed by the eqn. (11), for the case of an ML transition: where  $\Delta E_{MLCT}$  and  $\Delta E_{MMCT}$  are the positions of the MLCT and metal-to-metal (intervalence) transitions, respectively. Note that this procedure requires mainly the recording of the charge transfer transitions, and that the intervalence transition intervenes only by its position, which can be only approximately determined. On the other hand, this treatment considers only one metal-to-ligand or ligand-to-metal excited state, while in most conjugated molecules there are generally several closely lying such states, and their effects can be additive or subtractive according to the symmetry of the ligand orbitals.

$$V_{ab} = \frac{H_{ML} H_{ML'}}{2 \Delta E_{ML}} + \frac{H_{LM} H_{LM'}}{\Delta E_{LM}} \quad (9)$$

$$V_{ab} = \frac{H_{ML}^2}{2 \Delta E_{ML}} + \frac{H_{LM}^2}{\Delta E_{LM}} \quad (10)$$

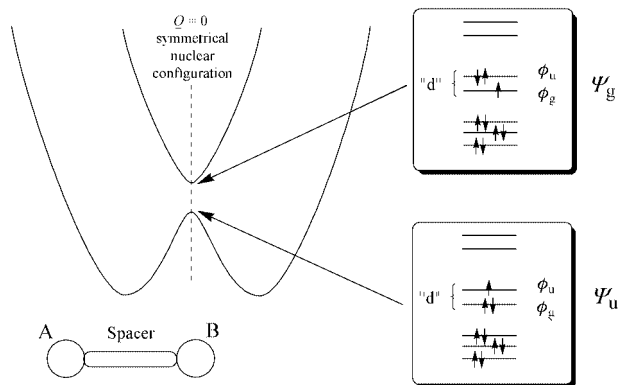
$$\frac{1}{\Delta E_{ML}} = \frac{1}{2} \left( \frac{1}{\Delta E_{MLCT}} + \frac{1}{\Delta E_{MLCT} - \Delta E_{MMCT}} \right) \quad (11)$$

Finally, let us mention that the mixed-valence literature frequently mentions “electronic communication” between redox sites, which is measured by the electrochemical wave splitting between the Ox–Ox/Red–Ox and Red–Ox/Red–Red couples. However, in most cases, this parameter is only weakly dependent on the true  $V_{ab}$  parameter. In the writer’s opinion, this use of wave splitting is very qualitative and should be discouraged.<sup>12</sup>

## 2.4 Theoretical descriptions and quantum chemical evaluations of the electronic coupling

The electronic interaction between metal sites linked by a bridging ligand is at the heart of electron transfer. In the avoided crossing region of Fig. 2 (left), if the system, because of its previous history, is initially in a localized state such as in Ru<sup>II</sup>–Ru<sup>III</sup>, it will evolve dynamically towards the other localized state Ru<sup>III</sup>–Ru<sup>II</sup>. But this evolution as a function of time is complex, and may involve states in which the bridging ligand is either oxidized or reduced. On the other hand, chemical intuition suggests that it should be modelled by a two-state description. This is conveniently performed by an effective Hamiltonian.<sup>13</sup> From a computational point of view, the  $V_{ab}$  parameter can be theoretically evaluated by several methods:<sup>13</sup> (i) a dynamic method, *i.e.* from the frequency of the most intense component of the time evolution when the system is prepared in a non-stationary state; (ii) an effective Hamiltonian method, in which one computes matrix elements such as  $\langle d_a | H_{\text{eff}} | d_b \rangle$ , where  $H_{\text{eff}}$  is the effective Hamiltonian, and  $d_a$  and  $d_b$  describe *pure metallic* wave functions, and (iii) by the “dimer splitting” method, *i.e.* from the energy difference between the two possible energies at the crossing point. The equivalence of these methods has been demonstrated elsewhere.<sup>13</sup> The following discussion is mainly based on the last method, because it requires only a static calculation of eigen vectors and eigen energies of the molecule, and thus can be performed in a straightforward way with commercial programs.

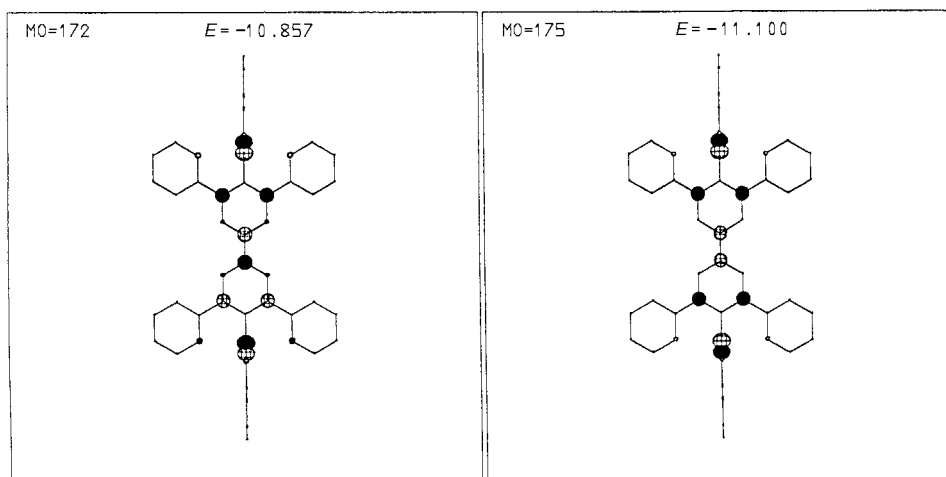
In principle, one should compute the total energy of the mixed-valence system for the two possible electronic states at  $Q = 0$  (see Fig. 4, showing in particular the distinction between *total* wave functions such as  $\Psi_g$ ,  $\Psi_u$ , and *monoelectronic*



**Fig. 4** The electronic interaction at the crossing point ( $Q = 0$ ) showing the principle of the “dimer splitting” evaluation of  $V_{ab}$ ; “d” designates molecular orbitals with preponderant d character centred on A and B metal sites.  $\Psi_g$  and  $\Psi_u$  are total electronic wavefunctions, while  $\phi_u$  and  $\phi_g$  are monoelectronic wavefunctions.

wavefunctions such as  $\phi_g$ ,  $\phi_u$ ).<sup>14–16</sup> However, in most of the cases an exact calculation, *i.e.* at the *ab initio* SCF level, taking into account electron correlation, is out of reach due to the size and complexity of the molecules. In addition, although the system is perfectly symmetrical, it is well known that artefactual symmetry breaking of the Hartree–Fock solutions may occur.<sup>14,16</sup> Thus, simpler methods based on one-electron levels are usually used. For instance, at the Extended Hückel level,  $V_{ab}$  is simply taken as half the energy difference between two orbitals having high weights on the metal atoms, and presenting opposite symmetries, such as  $\phi_g$  and  $\phi_u$  (Fig. 4).<sup>13</sup> Although crude, this method gives very satisfactory orders of magnitudes of the electronic coupling, and is particularly well adapted to qualitative chemically based discussions. An example of such orbitals is given Fig. 5. It is important to notice that the interaction is described by the *difference* in energy between these two orbitals, and not by the properties of a single orbital, even when it shows an important delocalization on the bridging ligand.

Of course, the parametrization of uncommon elements such as ruthenium raises difficulties, particularly the diagonal matrix element corresponding to the initial energy of the d orbitals. Furthermore, due to the principle of the Extended Hückel method, the effect of the environment on the metal atom (ancillary ligands) is not correctly reproduced, neither are the effects related to the charge distribution. But in some cases, it is possible to extract reasonable values for the diagonal matrix element from an SCF calculation, performed, for instance, at the ZINDO level, and to transfer it into the Extended Hückel calculation.<sup>17</sup>



**Fig. 5** Example of  $\phi_g$  and  $\phi_u$  orbitals defining the coupling in the “dimer splitting” method: the case of a cyclometallated complex of the dipyritylbenzene family, in a planar conformation, thus presenting an inversion center. (Reprinted with permission from ref. 17. Copyright 1998 American Chemical Society.)

At the SCF level, a simple but approximate extraction of  $V_{ab}$  from orbital energies is still possible if the calculation is made on the homovalent closed-shell system (*e.g.*  $\text{Ru}^{\text{II}}\text{--Ru}^{\text{II}}$ ). Through Koopman's theorem the orbital energies are indeed related to the two possible energies of the ionization product, *i.e.* the mixed-valence compound.<sup>14,16</sup> However, the most rigorous approach necessitates the full many-electron treatment with evaluation of total electronic energies, including correlation effects. At this level, two variants can be considered: (i) from adiabatic energy splitting (dimer splitting), *i.e.* calculating the energy difference between the two possible electronic states, and (ii) from the direct calculation of the matrix element  $\langle \Psi_a | H | \Psi_b \rangle$  where  $\Psi_a$  and  $\Psi_b$  represent diabatic total electronic wave functions. These wave functions correspond to the unperturbed basis states  $\text{Ru}^{\text{II}}\text{--Ru}^{\text{III}}$  and  $\text{Ru}^{\text{III}}\text{--Ru}^{\text{II}}$ , and can be obtained by a symmetry-broken SCF calculation.<sup>14</sup> They derive in particular from symmetry adapted wave functions such as  $\Psi_g$  and  $\Psi_u$  by the standard unitary transformation  $2^{-1/2}(\Psi_g \pm \Psi_u)$ .<sup>15,16</sup>

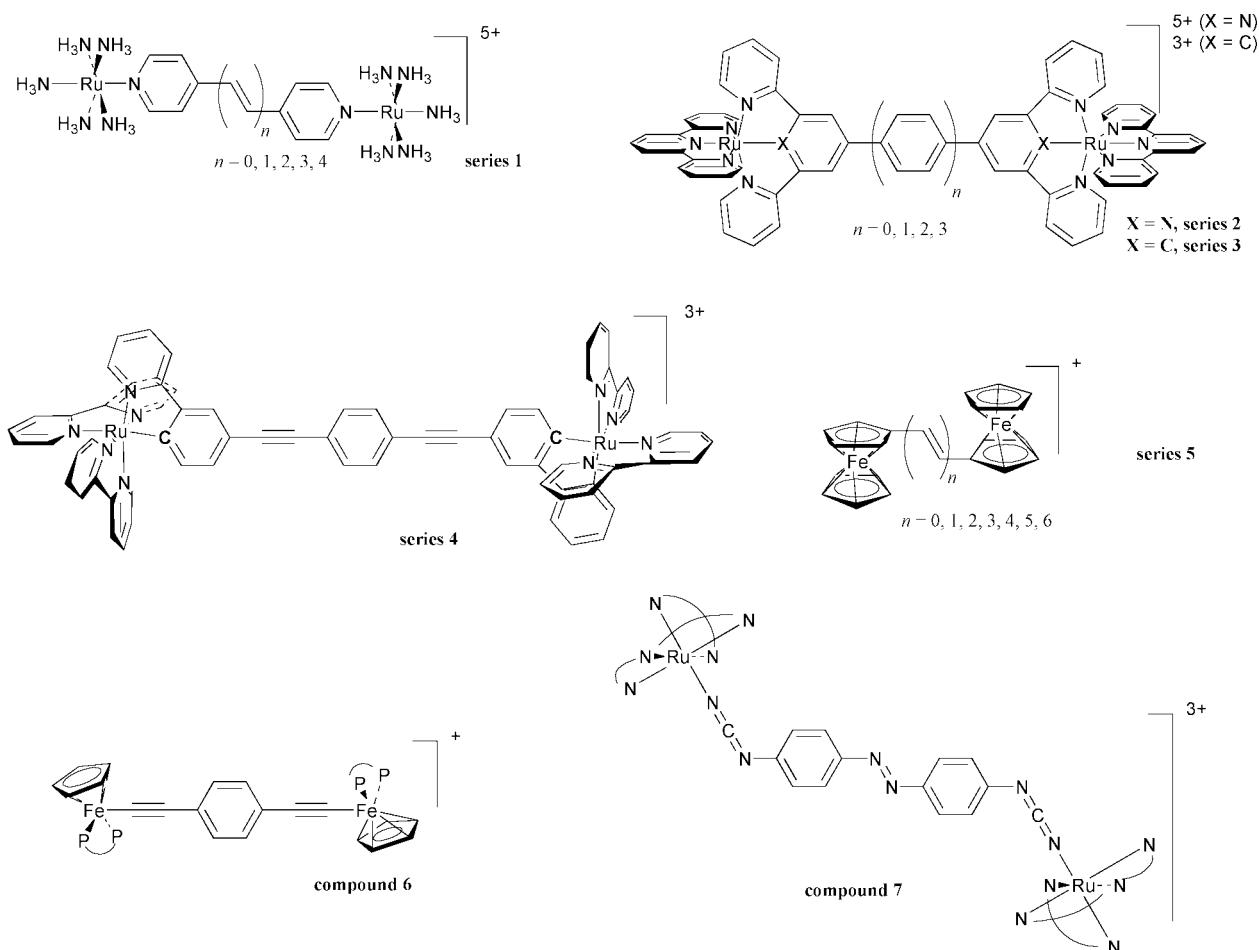
In principle, accurate values of metal–metal couplings can be obtained by these high-level quantum chemical calculations, but they appear as “black boxes” because they are performed on the complete system. Now, there is a need for pedagogical dissections showing the structural or energetic factors determining  $V_{ab}$ . For instance, a quantum mechanical calculation performed on a system in which one metallic site has been suppressed can give an approximation of one of the diabatic wave functions. These functions possess “tails” extending on to the bridging ligand, the inspection of which gives clues as to strategic places for performing substitutions and increasing their overlap. In other respects, the role of the bridging ligand can be uncovered by calculations performed on the free ligand, in order to identify its particular mode of interaction in the frame

of superexchange theory (either primarily by its LUMO, corresponding to genuine electron transfer across the ligand, or primarily by its HOMO, corresponding to hole transfer).

### 3 Chemical nature of mixed-valence compounds with large metal–metal distances

Historically, the study of molecular mixed-valence systems was triggered by Taube's seminal work on compounds such as  $[(\text{NH}_3)_5\text{Ru--pyz--Ru}(\text{NH}_3)_5]^{5+}$ , where pyz = pyrazine. This initiated the synthesis of a great variety of molecular mixed-valence compounds. Here we shall mention only the main families, a comprehensive survey being available elsewhere.<sup>12</sup>

From the point of view of the redox sites, ruthenium chemistry occupies a privileged position, owing to the great stability of its metal complexes, the ease of obtaining oxidation states II and III, and their kinetic inertness. In fact, these advantages are essentially true for ruthenium–pentaammine or –tetraammine systems, for which the redox potential is moderate (near 0 V vs. SCE). For ruthenium–tris(bipyridine) derivatives, the strongly  $\pi$  acceptor character of the ligand shifts the redox potential to high values (1 V or more), so that the III oxidation state becomes too reactive, and is subject to side reactions with the solvent or impurities. An interesting development of ruthenium chemistry makes use of cyclometallated compounds, *i.e.* compounds derived from the usual bipyridine or terpyridine ligands by replacement of a nitrogen by a formally negative carbon atom (Fig. 6). Such compounds again exhibit redox potentials over a moderate range, which facilitates equilibrium studies in which the two oxidation states coexist. Negatively charged ligands, such as cyanamido, also



**Fig. 6** Examples of inorganic mixed-valence compounds in which long-distance intervalence electron transfer can occur. For ruthenium complexes, the mixed-valence state is  $\text{Ru}^{\text{II}}\text{--Ru}^{\text{III}}$ ; for ferrocene systems (series 5), it is  $\text{Fe}^{\text{II}}\text{--Fe}^{\text{III}}$  (ferrocene–ferricinium); for compound 6, it is also formally  $\text{Fe}^{\text{II}}\text{--Fe}^{\text{III}}$ .

shift the redox potential towards moderate values, and, in addition, their use as a bridging unit leads to very high electronic couplings.

Another great family of redox sites is provided by organometallic moieties of the ferrocene type. They were developed shortly after ruthenium compounds, because the facile oxidation of ferrocene to ferricinium had attracted early attention, in particular for electrochemical studies. The functionalisation of ferrocene is now well mastered. Note, however, that the oxidized form of ferrocene is subject to reactions with chloride ions or oxygen (!) leading to decomplexation. More recently, many organometallic compounds with (dppe)Cp\*Fe moieties have been described [dppe = ethylenebis(diphenylphosphine)]. Their chemistry is flexible enough to allow association with various spacers.

The spacer linking the redox sites can be constituted by various conjugated groups used alone or in conjunction. The simplest solution is to rely on conjugated double bonds (polyene fragment), but when the size of the spacer is increased, one is limited by the decreasing stability and the occurrence of side reactions and complicated isomerizations. Triple bonds have been used, and proved surprisingly stable as polyene fragments (C≡C)<sub>n</sub> up to *n* = 4 in mixed-valence chemistry. Polyphenylene spacers are very stable, but possess an orientational disorder since the adjacent phenylene groups cannot be planar. They have been used in up to three phenylene units. In fact, the combination of several types of conjugated units has proved fruitful, in particular the association of phenyl and double bonds (polyphenylenevinylene) and of phenyl and triple bonds (polyphenylene-ethynylenes). These associations appear the best solution for obtaining very long and stable spacers. (Their efficiency in transmitting electronic effects is discussed in Section 4.1.)

The general synthetic methods for obtaining metal-based mixed-valence compounds can be broadly divided in two classes:<sup>12</sup> (i) a “classic” strategy, in which the bridging ligand is prepared, and later complexed by the metal site. The drawback is the decreasing solubility of the bridging ligand when the size increases. (ii) A “modular” strategy using a metal complex as building block. This strategy is common in organometallic chemistry where the free anionic ligands (*e.g.* cyclopentadienyl anion) cannot be easily manipulated. It has proved extremely efficient in recent years for the synthesis of long systems, because the organometallic synthon can frequently be used in classic organic reactions, and the solubilities do not vary very much upon functionalization.

Finally, since most synthetic methods yield the binuclear complex in the homovalent state (Ru<sup>II</sup>–Ru<sup>II</sup>, or Fc–Fc), the final stage is the controlled oxidation to the mixed-valence state. This is performed either electrochemically or chemically by a variety of redox agents [chlorine, cerium(IV), iodonium compounds, *etc.*].

## 4 Results for selected series of compounds

### 4.1 The experimental decay law of electronic interaction with distance in binuclear metal complexes

In this paragraph, we focus on *series of compounds* that allow the determination of the rate of decay of *V*<sub>ab</sub> with the distance separating the metal sites. In most cases, it follows, or nearly follows, an exponential law as given by eqn. (12). Ideally, an interesting system, in which the spacer acts as a good molecular wire, should exhibit a strong coupling even for large distances, *i.e.* a low *γ* and a high *V*<sub>ab</sub><sup>0</sup>. While an extensive review is available elsewhere,<sup>12</sup> we describe here only the more representative examples, which are ranked by type of end group. They are illustrated in Fig. 6. In the following, we indicate the

ligand of the coordination sphere to which the spacer is attached, *e.g.* “py–” means that the pyridine ligand is the site of attachment of the spacer.

$$V_{ab} = V_{ab}^0 \exp(-\gamma R_{MM}) \quad (12)$$

**4.1.1 (NH<sub>3</sub>)<sub>5</sub>Ru(py–) series.** The simplest complex is the association of two such end groups without a connector, *i.e.* [(NH<sub>3</sub>)<sub>5</sub>Ru–4,4′-bipy–Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>*n*+</sup>. This is one of the most studied complexes as a representative example of a weakly coupled (class II) mixed-valence system.<sup>1</sup> In particular, it allows the study of several original or intriguing effects: multiple intervalence transitions, contributions of high-frequency vibrations, and effects of unsymmetrical solvation. This is also the longest mixed-valence complex for which electroabsorption spectroscopy (Stark effect) has been performed.<sup>10</sup> This experiment provided the value of the change in adiabatic dipole moment (Δ*μ*<sub>12</sub>) associated with the intervalence transition: while the absolute value is very large (*ca.* 28 D), the Δ*μ* value is about one half of the theoretical value for a full charge transfer over 11.3 Å.

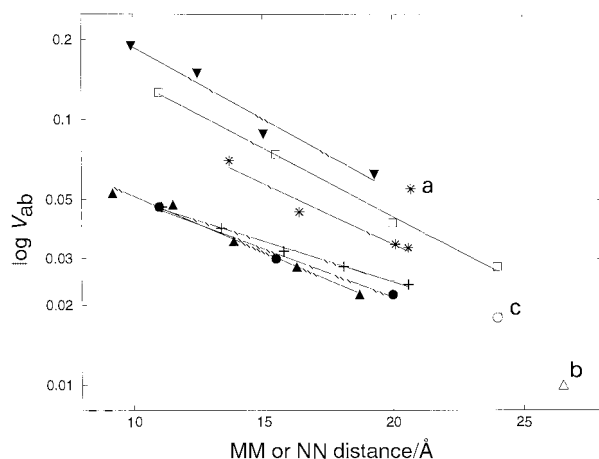
Inserting one or several conjugated double bonds gives rise to complexes of α,ω-dipyridylpolyenes, py–(CH=CH)<sub>*n*</sub>–py, the first examples (*n* = 0, 1) being described by Sutton and Taube,<sup>1</sup> and the longer ones (*n* = 2–4) by Launay *et al.*<sup>18</sup> (series **1**, Fig. 6). Analysis of the intervalence transitions showed a steady decrease of the *V*<sub>ab</sub> coupling term according to an exponential law, within the uncertainties of the measurements. For the longest systems, the intervalence transitions were increasingly ill-resolved. However, the inclusion of furan and thiophene heterocycles in place of two double bonds improved the resolution, probably for reasons of better coplanarity and rigidity. For series **1**, the experimental decay slope *γ* was found to be 0.070 Å<sup>–1</sup>.

Theoretical values of the coupling were obtained by extracting the *V*<sub>ab</sub> values from an Extended Hückel calculation, either by the “dimer splitting method” or by the Effective Hamiltonian technique.<sup>13</sup> The order of magnitude of the coupling was satisfactorily reproduced, and the role of bond length alternance as a limiting factor in the long-distance transmission of electronic coupling was recognised.

An alternative theoretical treatment of α,ω-dipyridylpolyenes complexes was proposed in 1990 by Reimers and Hush, in which the quantum calculation is performed at the CNDO level with an empirical adjustment of the d levels of ruthenium with respect to the bridging ligand orbitals. This calculation gave a higher decay slope of –0.13 Å<sup>–1</sup>. In a more recent work, the explicit treatment of the solvent allowed reproduction of experimental couplings within 25% of experimental data, with a decay slope of –0.127 Å<sup>–1</sup>.<sup>19</sup>

The insertion of a triple bond was performed by Sutton and Taube.<sup>1</sup> Curiously the *V*<sub>ab</sub> coupling was found smaller through diprydilacetylene than through diprydylethylene, a fact attributed to the almost free rotation of the two pyridine rings with respect to each other.

**4.1.2 (bpy)<sub>2</sub>(Cl)Ru(py–) and (bpy)<sub>2</sub>Ru(bpy–) series.** Complexes with (bpy)<sub>2</sub>(Cl)Ru moieties bridged by 4,4′-bipyridine, or bipyridylethylene were prepared by Meyer *et al.*, but unfortunately, they exhibit lower couplings when compared to the analogous ruthenium(pentaammine) compounds.<sup>1</sup> This is attributed to the competitive effect of π-acceptor ancillary ligands that drain the electron density away from the bridging ligand. An interesting exception, reported by Lehn *et al.*,<sup>20</sup> is the mixed-valence complex of Ru(bpy)<sub>2</sub> bridged by 1,10-bis[4′-methyl(2,2′-bipyridyl)]-3,8-dimethyldecapenta-1,3,5,7,9-ene, *i.e.* with 5 double bonds constituting the spacer between the 2,2′-bipyridine ligands. Hush’s analysis of the intervalence transition gave *V*<sub>ab</sub> = 0.018 eV for a 24 Å metal–metal distance, which falls in the continuation of several series (see Fig. 7).



**Fig. 7** Decay law for the electronic interaction with distance for compounds belonging to various series.  $V_{ab}$ /eV (on a log scale) is plotted against the through-space metal–metal distance, or the nitrogen–nitrogen distance in the case of fully organic systems. +: ruthenium bipyridylpolyene complexes (series 1); ●: ruthenium bis(terpyridyl) complexes (series 2); □: ruthenium bis(cyclometallated) complexes, dipyritylbenzene family (series 3); \*: ruthenium bis(cyclometallated) complexes, phenylpyridine family (series 4); ▲: bis(ferrocenyl) polyenes (series 5); ▼: organic systems with bis(4-methoxyphenyl)phenylamine sites (series 9, Fig. 9). Additional measurements: a: bis(cyclometallated) complex (series 4) with diethynylanthracene as spacer; b: bis(ferrocene) with three phenylene and four vinylene units as spacer; c: bis[ruthenium(trisbipyridyl)] with 5 double bonds as spacer.

**4.1.3 (terpy)Ru(terpy–) series.** These complexes are made from a bridging ligand in which two terpyridine groups are either directly connected end-to-end, or *via* a polyphenylene spacer ( $C_6H_4$ )<sub>n</sub>,  $n = 1, 2$  (series 2, Fig. 6). Starting from the ruthenium(II) complexes, oxidation by Ce(IV) in acetonitrile yielded the mixed-valence species, and Hush's analysis gave the corresponding  $V_{ab}$  couplings.<sup>12</sup> The decay slope for the  $\ln(V_{ab})$  vs.  $R$  plot was  $-0.084 \text{ Å}^{-1}$ . The high values of the redox potentials (*ca.* 1.3 V vs. SCE) were however a drawback of this series, since the oxidized species were not stable for long periods and titrations had to be performed rapidly. Cyclometallated species (see below) represent a significant improvement in this respect.

**4.1.4 (terpy)Ru(dpb–) series** (dpb = 1,3-dipyridylbenzene) and (terpy)Ru(bdmab–) [bdmap = bis(dimethylaminomethyl)benzene]. The first complexes, prepared by Collin and Sauvage, are structurally similar to those of the bis(terpy) family, but with the nitrogen atom of the central ring replaced by a carbon atom (cyclometallated species). The spacer between the dipyritylbenzene coordination sites can be made of 0 to 3 phenylene units, with the metal–metal distance ranging from 11 to 24 Å (series 3, Fig. 6). Starting from ruthenium(II), the oxidation occurred more easily (*ca.* 0.5 V vs. SCE) than for the corresponding bis(terpyridine) complexes, and a much stronger coupling was observed for the mixed-valence species.<sup>17</sup> However, the rate of decay in the  $\ln(V_{ab})$  vs.  $R$  plot was faster ( $-0.118 \text{ Å}^{-1}$  instead of  $-0.084 \text{ Å}^{-1}$ ). This key observation is discussed in more detail in Section 4.2. The mechanism of electronic coupling, and, in particular, the effect of replacing a nitrogen atom by a carbon, could be addressed by molecular orbital calculations.<sup>17</sup> It was found that the theoretical predictions were very sensitive to the energy of the Ru(4d) orbitals, which unfortunately are somewhat arbitrarily positioned in conventional Extended Hückel calculations. However, with the help of ZINDO method, it was possible to justify the choice of the ruthenium orbital energies, and to reproduce the main features of the series.

The bis(dimethylaminomethyl)benzene ligand ("pincer") developed by van Koten is also an interesting cyclometallating ligand, structurally similar to dipyritylbenzene. With two such complexing parts connected back-to-back ("bis-pincer"), it is

possible to prepare strongly coupled bimetallic complexes with a metal–metal distance of 10.8 Å.<sup>21</sup> An intense intervalence band ( $\epsilon = 33000 \text{ mol}^{-1} \text{ l cm}^{-1}$ ) was observed, and computing  $V_{ab}$  from the Hush formula gives 0.165 eV, *i.e.* more than for the analogous bis(dipyridylbenzene) complex. (Considering the system as class III would give  $V_{ab} = 0.33 \text{ eV}$ .)

**4.1.5 (bpy)<sub>2</sub>Ru(pp–) series.** These cyclometallated species are based on 2-phenylpyridine as the complexing part. The spacer can be one or two triple bonds or diethynylaryl groups (aryl = 9,10-anthrylene, 2,5-thienylene, or 1,4-phenylene), constituting series 4 (see Fig. 6). As for cyclometallated complexes of the dipyritylbenzene family, the oxidation is easy (*ca.* 0.5 V vs. SCE), and the intervalence transitions are relatively intense, although partly overlapped by a nearby charge transfer transition of ruthenium(III).<sup>12</sup> For a given length, the obtained couplings are generally intermediate between the ones of the bis(terpy) and dipyritylbenzene families, and the decay slope is  $-0.104 \text{ Å}^{-1}$  if the complex with a diethynylanthracene spacer is excluded. This last one exhibited indeed a particularly strong coupling, which is discussed below (Section 4.2).

**4.1.6 (Cp)Fe(Cp–) series.** A series of  $\alpha,\omega$ -diferrocenylpolyenes with  $n = 1$  to 6 conjugated double bonds have been prepared and oxidized electrochemically in dichloromethane by Launay *et al.*<sup>22</sup> (series 5, Fig. 6). Intervalence transitions yielded the electronic coupling terms as a function of the number of double bonds. Although the decrease with distance was essentially exponential, a small but significant deviation was observed for  $n = 3$ , suggesting that there could be two regimes for the decay law, one from 1 to 3 double bonds, and the other one beyond 3. Ferrocene-containing molecules present, however, some drawbacks, such as low solubility and a tendency to decompose upon oxidation. Substituted ferrocenes, in particular pentamethylferrocenes, are interesting alternatives. With a spacer made from 3 phenylene and 4 vinylene units, an intervalence band has been obtained, corresponding to a coupling of 0.01 eV for a metal–metal distance of 26.5 Å.<sup>12</sup>

## 4.2 Theoretical rationalizations for the binuclear metal complex series

Most of the results on series of compounds can be summarised as shown in Fig. 7 where the key parameter  $V_{ab}$  (log scale) is plotted against  $R_{MM}$ . In fact, the coupling is expected to depend essentially on the number of bonds connecting the metal atoms, but since we are dealing with almost linear systems, the true metal–metal distance is also a good parameter. The coupling usually displays an exponential decrease (except in the case of bis(ferrocenyl)polyenes, for which a small but significant departure has been observed, as mentioned above). This behaviour is common for a number of processes ultimately linked to orbital overlap, such as electron and energy transfer rate constants, magnetic coupling, electronic transparency of molecules in nanojunctions,<sup>23</sup> *etc.*

A simple tight-binding model can be used to describe a donor–bridge–acceptor system, and can be adapted to mixed-valence systems made of two terminal sites and several repeat units. It uses three parameters:  $\alpha$ , the coupling between equivalent repeat units constituting the bridge,  $\beta$  the coupling between the last unit of the bridge and one terminal site, and  $a$ , the energy difference between terminal and bridge sites (Fig. 8).<sup>12,13</sup>

This model allows the determination of the effective coupling  $V_{ab}$  and of its decay with distance. It was initially formulated in a perturbational way, but was later developed exactly. The complete analysis predicts a wide variety of behaviour according to the values of the parameters: slow or fast decay, exponential or non-exponential law and oscillations.<sup>13</sup> In a

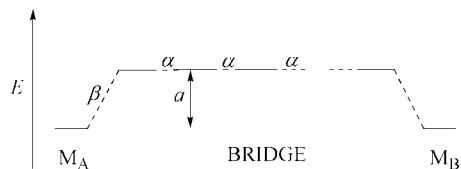


Fig. 8 The tight-binding model with  $\alpha$ ,  $\beta$ , and  $a$  parameters.

refinement of the original model, the effect of alternation, *i.e.* the existence of two different intra-bridge couplings  $\alpha_1$  and  $\alpha_2$  was also considered.<sup>13</sup> Regarding the frequent occurrence of the exponential decay, this is general behaviour when, as is usual with most conjugated bridges used in mixed-valence chemistry, the metal energy levels fall in the “gap” of the bridge backbone, *i.e.* they are far from resonance.

The most striking point from Fig. 7 is that many compounds with very diverse structures fall in the same area, giving similar  $V_{ab}$  values and decay slopes in the range 0.07 to 0.10 Å<sup>-1</sup>. Cyclometallated compounds, on the other hand, exhibit a special behaviour, characterised by a larger  $V_{ab}$ , but also a larger decay slope. This is particularly true for compounds where the coordinating site belongs to the bipyridylbenzene family, but the trend is also very clear with compounds of the phenylpyridine family. To use the simple tight-binding model above as an explanatory tool, it is necessary to have at least a rough idea of the change in the formal  $\alpha$ ,  $\beta$ ,  $a$  parameters from one compound to the other.

According to molecular orbital calculations, the main difference between bis(terpyridyl) complexes and the corresponding cyclometallated ones depends on the tail of the wave functions with mainly metal character. In the case of cyclometallated compounds, they have greater extension on the carbon atom located *para* to the ruthenium–carbon bond, thus ensuring better communication with the bridge.<sup>17</sup> In the frame of the simple model above, this is equivalent to an increase in  $\beta$ , which leads to an increase in  $V_{ab}^0$ , and an increase in the  $\gamma$  decay coefficient.

Thus, it does not seem possible, in general, to win with  $V_{ab}^0$  and  $\gamma$  at the same time.<sup>13</sup> In other words, the  $V_{ab}^0$  vs.  $\gamma$  competition appears inherent to the structure of any compound made from repeat units. The above tight-binding model is however very crude, because assigning just one energy level to one repeat unit does not take into account the detailed structure of the latter. In fact, each of these units may exhibit several energy levels with different symmetries. An explicit treatment taking into account this complexity is possible, and has been performed recently for the related problem of metal–molecule–metal nanojunctions.<sup>23</sup>

Finally, it is remarkable that the incorporation of anthracene in the spacer can markedly increase the coupling, as shown on Fig. 7 (compound marked “a”). This could be related to the ease of oxidation of the anthracene unit (high energy HOMO) favouring superexchange through hole-transfer.

### 4.3 Particularly strong couplings

A number of compounds exhibit surprisingly high couplings. They are not generally members of a series such as those described above, and so we shall concentrate on the absolute values of the couplings, and not on the  $\gamma$  factor. These compounds raise fundamental problems because strong coupling in a compound with a large metal–metal distance necessarily involves an extensive delocalization on the bridge. This can be easily shown by inspection of orbitals defining the coupling. Thus, the validity of the standard approaches based on two-state models (original Hush treatment, GMH model) can be questioned.

#### 4.3.1 Organometallic systems with carbon-rich bridges.

Organometallic species exhibiting intervalence transitions through bridges essentially made of carbon atoms have been described by Lapinte and Paul. The end group is (Cp\*)(dppe)Fe(C≡C)–, where dppe = ethylenebis(diphenylphosphine), and the spacer is either a phenylene unit or two triple bonds. In terms of *bridging ligand* (see again Fig. 1 for the distinction with respect to spacer) it is either 1,4-bis(ethynyl)benzene (metal–metal distance 11.9 Å), or octatetrayne (metal–metal distance 12.6 Å),<sup>24</sup> *i.e.* a chain of eight sp-hybridized carbon atoms. The synthesis gives initially the 18e–18e species [formally Fe(II)–Fe(II)], which can be quantitatively oxidized to the 35e mixed-valence species, thanks to a large comproportionation constant (wave splittings 0.26 and 0.43 V respectively).

For the complex bridged by 1,4-bis(ethynyl)benzene (compound 6, Fig. 6), the experimental evidence (Mössbauer, EPR, IR) shows borderline behaviour between class II and III. The electronic coupling is then either 0.064 eV (class II) or 0.31 eV (class III).<sup>24</sup> For the complex bridged by octatetrayne, class III behaviour appears most likely from the IR spectrum and the sharp intense intervalence transition, giving  $V_{ab} = 0.32$  eV.<sup>24</sup> The treatment as class II (less likely) would give 0.09 eV. Thus, there is potential for completely carbon bridges, taking into account that longer binuclear systems have been described (but not yet in the case of mixed-valence compounds).

#### 4.3.2 Compounds with bis(cyanamido) bridging ligands.

The bridging ligand dicyanamidobenzene and its dichloro- and tetrachloro-substituted variants has been extensively studied by Crutchley *et al.*<sup>25</sup> The first reported compounds had (NH<sub>3</sub>)<sub>5</sub>Ru terminations. The measurement of intervalence transitions is complicated by the overlap with intense LMCT bands of the ruthenium(III) chromophore. An intriguing effect is the great sensitivity of the intervalence transition to the solvent, showing that the coupling is much greater in acetonitrile than in D<sub>2</sub>O. This is attributed to the specific interaction between the solvent and ammine protons. In acetonitrile, the dicyanamido ligand gives a 980 cm<sup>-1</sup> (0.122 eV) coupling from Hush’s formula.<sup>25</sup> It is possible to prepare longer homologues of dicyanamidobenzene, such as the 4,4’-dicyanamidobiphenyl dianion, with the metal–metal distance reaching 17.2 Å. The corresponding complex gives a 400 cm<sup>-1</sup> (0.050 eV) coupling.

With (NH<sub>3</sub>)<sub>4</sub>(py)Ru and (NH<sub>3</sub>)<sub>3</sub>(bpy)Ru moieties and dicyanamidobenzene as bridging ligand, intervalence transitions give  $V_{ab}$  values through Hush’s equation in the 800–1100 cm<sup>-1</sup> range (0.1–0.13 eV), while estimations through the CNS model give much higher values (0.2 to 0.4 eV).<sup>25</sup> But as mentioned above, this simple application of the CNS model relies on just one LMCT excited state, involving only the ligand HOMO, while in principle all the ligand orbitals can contribute.

Using (bpy)(terpy)Ru moieties and the dicyanamido ligand gives a very appealing result. The mixed-valence ion presents an intervalence band at 1090 nm, and the authors assign the system to class III, yielding thus a high  $V_{ab}$  coupling (half the optical energy, *i.e.* 0.57 eV).<sup>26</sup> However, since the band is moderately intense ( $\epsilon = 5\,600$  mol<sup>-1</sup> l cm<sup>-1</sup>), a class II nature could also have been considered, and in such a case, from the published values, Hush’s equation would give a 0.058 eV value. (For such complexes, treating them either as class II or class III systems results in large changes in  $V_{ab}$ .)

Finally, very recently, the complex bridged by the [4,4’-azobis(phenylcyanamido)]<sup>2-</sup> ligand has been shown to exhibit a very strong coupling (0.32 eV), since it exhibits class III behaviour for a 19.5 Å metal–metal distance (compound 7, Fig. 6).<sup>26</sup> This unprecedented efficiency of a bridging ligand for such a distance is both puzzling and exciting. The proposed explanation is that this bridging ligand intervenes by two superexchange processes, *i.e.* hole transfer, through its HOMO, and electron transfer, through its LUMO. The argument is



plausible since the bridging ligand can be viewed as a donor–acceptor–donor system, because it combines the cyanamido group (electron donor) and a central azo group (electron acceptor).

Thus, bridging ligands of the bis(cyanamido) type exhibit record values for the electronic coupling. In a related way, they also promote strong intramolecular antiferromagnetic coupling when the binuclear complexes are fully oxidized, *i.e.* to the Ru<sup>III</sup>–Ru<sup>III</sup> state.

More generally, these two types of highly coupled systems (involving carbon-rich or dicyanamido bridges) raise interesting theoretical problems. Quantum chemical calculations should help in understanding the fundamental reasons for such behaviour. Clearly, the bridging ligand plays a subtle role by virtue of the richness of its electronic structure, and the description of the system must go beyond the simple tight-binding model evoked above (Section 4. 2). It seems that the efficiency of some of these compounds comes from a precise tuning of the bridging ligand energy levels, with respect to the metal ones. Finally, for class III systems, extensive mixing of bridge and metal orbitals certainly occurs in both the ground and excited state, so that the intervalence transition should have some character of a bridging ligand–bridging ligand transition.

#### 4.4 Organic mixed-valence compounds

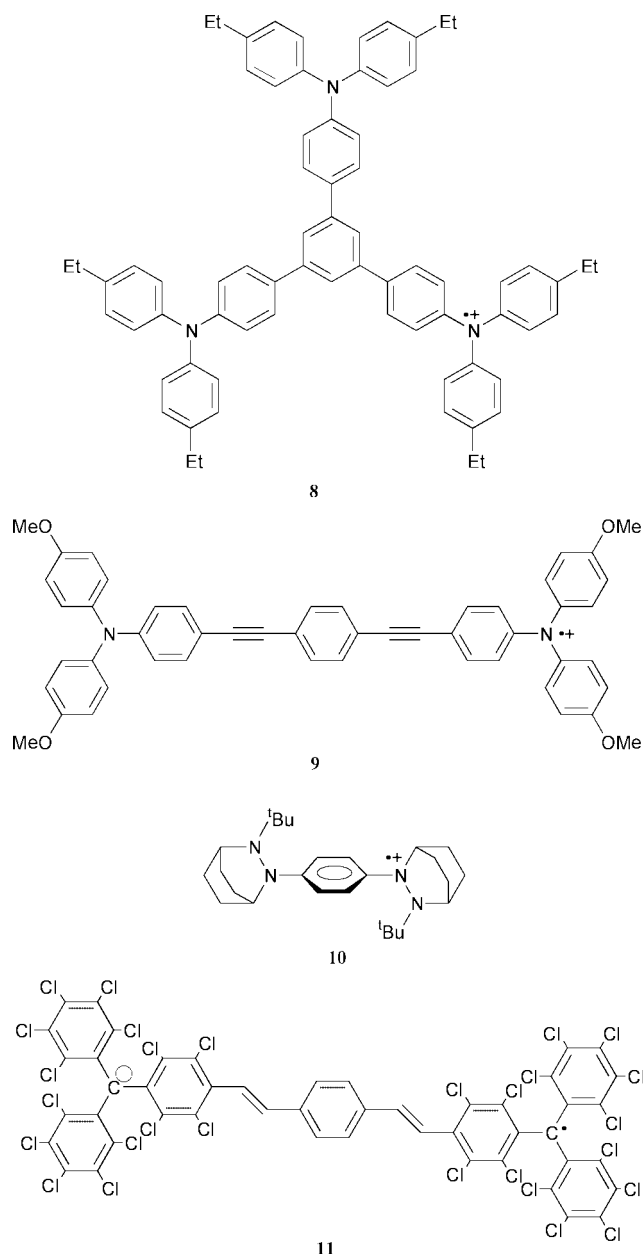
Mixed valence exists also in organic chemistry, although its occurrence was recognised later than in the case of inorganic compounds. This comes from the fact that one-electron processes are less common in organic chemistry, and that the notion of redox site is not so obvious. However, a number of systems with the general topology of two (or more) redox sites linked by a conjugated spacer can be found (see Fig. 9). Representative examples can be found in the review by Nelsen.<sup>27</sup>

A general difficulty in organic mixed-valence system is the natural tendency of the redox sites to exhibit extensive delocalisation on several atoms, contrary to the case of coordination compounds where the redox process concerns mainly the transition metal atom. Thus, in a redox site such as TTF (tetrathiofulvalene), the removal of one electron giving the TTF<sup>+</sup> radical cation, affects the whole structure, and is best described as the depopulation of a delocalised HOMO. On the other hand, more experimental methods are available in practice, in particular EPR which is well adapted to the determination of ground-state electron delocalisation and electron dynamics.

Focusing as above on really long systems, we first consider examples in the chemistry of bis(triarylamines). When properly substituted in the *para* position with respect to nitrogen, they can be reversibly oxidized to radical cations, and mixed-valence behaviour is observed when several sites are present.

Several compounds with two or three triarylamine sites have been studied by Van der Auweraer *et al.* (*e.g.* **8** Fig. 9).<sup>28</sup> This work showed that mixed-valence theory can be expanded to three-site systems, but the couplings were modest (0.025 eV for 12.5 Å) because the redox sites were connected through the *meta* position around a central site. The couplings could be reproduced by AM1 calculations performed on the neutral systems, using the dimer splitting of mono-electronic levels (*i.e.* functions such as  $\phi_g$  and  $\phi_u$ , see Section 2.4).

A series of analogous compounds, with nitrogen-to-nitrogen distances of up to 19 Å have been prepared by Lambert and Nöll using triple bonds and phenylene groups as spacers (series **9**, Fig. 9).<sup>29</sup> Intervalence transitions were exploited by a variant of eqn. (3) to yield nitrogen–nitrogen electronic couplings. The couplings are on average stronger than for inorganic mixed-valence compounds, still reaching 0.06 eV for a 19 Å nitrogen–



**Fig. 9** Some organic mixed-valence compounds: **8** is based on bis(4-ethylphenyl)phenylamine sites, series **9** is based on bis(4-methoxyphenyl)phenylamine sites with various spacers, and **10** on hydrazine sites. For **8**, **9**, and **10**, mixed-valence forms are generated upon partial oxidation to radical cations. Compound **11** is based on perchlorinated triphenylmethyl radical sites, and its mixed-valence form is generated upon partial reduction.

nitrogen distance. They even exceed the record values observed in the (terpy)Ru(dpb<sup>−</sup>) series (see Section 4. 1 above, and Fig. 7), but the rate of decay of  $V_{ab}$  with distance is similar (slope  $-0.12 \text{ Å}^{-1}$ ). Here also satisfactory calculations of the couplings were obtained at the AM1 level for the neutral forms.

As a result of the strength of the coupling, shorter systems exhibit behaviour close to that of class III. A detailed investigation of the intervalence band shape reveals a truncated profile, which is explained by the geometrical characteristics of the potential energy curves when the system is class III or borderline between class II and III.<sup>27</sup>

Substituted hydrazines constitute another interesting redox group. The oxidation of one hydrazine group of a bis(hydrazine) compound to the radical cation state generates mixed-valence compounds (see **10**, Fig. 9). The hole on the oxidized hydrazine unit can be delocalized on the two bonded nitrogen atoms. Since only one of them is connected to the bridge, the  $V_{ab}$  coupling is rather small, and localization (class II) occurs. In addition, the  $\lambda$  parameter is higher than for metal complexes, so that the

thermal electron transfer rate constant is rather slow, and falls in the EPR time window. Consequently, such systems allow the study of *both thermal and optical electron transfer*.<sup>30</sup> It is then possible to refine the description of the potential energy surface, for instance by showing the necessity of adding a quartic term in the  $E = f(Q)$  curves.<sup>30</sup> Interestingly, when the spacer is anthracene, the electron transfer in  $[\text{Hy}-\text{An}-\text{Hy}]^+$  (Hy = hydrazine, An = anthracene) is particularly fast. As for mixed-valence inorganic complexes [see Sections 4.1 and 4.2 about the  $(\text{bpy})_2\text{Ru}(\text{pp}-)$  series], this special effect of anthracene appears to be linked to its ease of oxidation. In the framework of superexchange, there is indeed an extensive mixing of the two basis states,  $\text{Hy}^+-\text{An}-\text{Hy}$  and  $\text{Hy}-\text{An}-\text{Hy}^+$ , with a third state,  $\text{Hy}-\text{An}^+-\text{Hy}$ , and this dramatically increases the coupling.

Carbon radical chemistry also offers opportunities for obtaining mixed-valence systems. Thus stable perchlorinated radicals of the triphenylmethane type can be reduced to anions, and constitute isoelectronic analogues of triphenylamine radical cations and neutral triphenylamine systems respectively. Veciana *et al.* have prepared a variety of such compounds with carbon-to-carbon distances reaching 19 Å, where the spacer is made of phenylene rings of various topologies (*meta*, *para*) or phenylene–vinylene units (see **11**, Fig. 9).<sup>31</sup> Intervalence transitions have been observed, but in addition, EPR measurements are rewarding, due to the tendency of these radicals to display well defined spectra with exploitable hyperfine structures. This has allowed the determination of the thermal electron transfer rate, and its variation with temperature, thus ultimately yielding the activation barrier for electron hopping. As for the hydrazine compounds discussed above, the simultaneous determination of thermal and optical electron transfer allows a complete investigation of the electron transfer process, but for a longer distance in the present case. The thermal activation energy for electron transfer is appreciably lower than  $\frac{1}{4}$  of the optical energy. The influence of topology can also be ascertained accurately, by comparing compounds with the radical sites connected either *meta* or *para* around a central phenylene unit.<sup>31</sup>

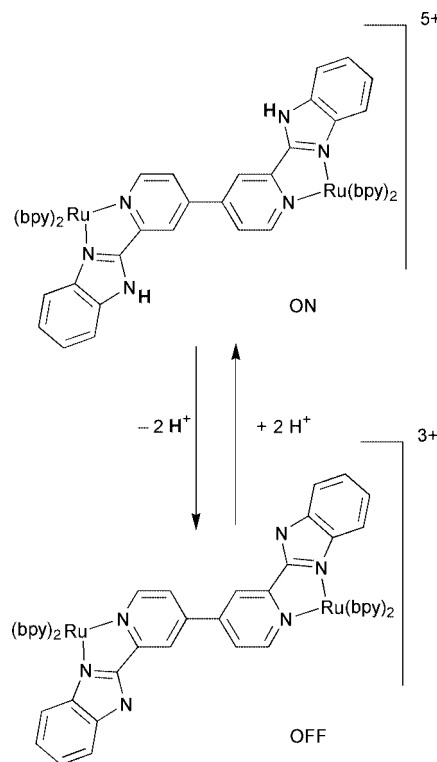
## 5 An application of long-distance intervalence electron transfer: molecular switching

The molecular switch has been from the beginning one of the challenges of molecular electronics with the aim of controlling electron transfer across a molecule, ideally in a binary way (*i.e.* ON/OFF). However the expression “molecular switch/switching” has been frequently used in a loose sense to designate any reversible change in a molecule able to exist in two states (conformational change, excitation, protonation, isomerization, *etc.*). In this paragraph, we shall use a definition based on a strict analogy with an electrical switch, *i.e.* the molecular switch must (i) undergo an intramolecular electron transfer (or transport) process, (ii) exist in two distinct states (ON/OFF) with possible conversion of one into the other by a perturbation, and stay in a given state once the perturbation has ceased. The two states need not possess an infinite lifetime, but it must be long enough so that significant characterizations can be performed independently.

Intervalence transitions are useful probes to monitor properties (i) and (ii), bearing in mind that such studies, performed in solution, can only test the basic principles of the design of a molecular switch, but do not lead to a useful device.

The early examples were provided by chemical perturbation of the bridging ligand in mixed-valence compounds. Thus, the effect of protonation was reported by Haga *et al.* in 1991, using the 2,2'-di-2-pyridylbibenzimidazole ligand ( $\text{bpimH}_2$ ). Upon deprotonation, the intervalence transition gains in intensity for mixed-valence complexes of the  $\text{Ru}^{\text{II}}-\text{Ru}^{\text{III}}$  or  $\text{Os}^{\text{II}}-\text{Os}^{\text{III}}$  type; the  $V_{\text{ab}}$  coupling increasing by a factor 4 to 6. Conversely, with

the 2,2'-bis(benzimidazol-2-yl)-4,4'-bipyridine ligand ( $\text{bbbpyH}_2$ ), deprotonation dramatically weakens the metal–metal coupling to the point that the intervalence band is no longer detectable (Fig. 10).<sup>32</sup> These changes can be explained by the variations in orbital energies of the bridge.



**Fig. 10** Switching by protonation–deprotonation in the case of a complex of 2,2'-bis(benzimidazol-2-yl)-4,4'-bipyridine ( $\text{bbbpyH}_2$ ).<sup>32</sup>

With 4,4'-azopyridine as bridging ligand, the effect is more complex, because protonation in fact leads to an intramolecular redox reaction, converting the bridging ligand into 1,2-di-4-pyridylhydrazine. Intervalence transition measurements show that electron transfer occurs across 4,4'-azopyridine, but is suppressed across 1,2-di-4-pyridylhydrazine.<sup>33</sup>

With 2,6-diferrocenylanthracene, it is possible to use the Diels–Alder addition of tetracyanoethylene (TCNE) to modify the electronic structure, and thus change the intramolecular ferrocene–ferricinium coupling. But in contrast to these expectations, the  $V_{\text{ab}}$  parameter does not vanish upon adduct formation: it decreases by only 40%.<sup>33</sup> A detailed investigation of the relevant molecular orbitals explains the weakness of the switching effect by  $\sigma-\pi$  mixing.

Photochemistry is however the best method to force a molecule to evolve in a controlled way from one state to another. To obtain a switching effect in the sense defined here, the electronic structure must undergo a profound change, with a great modification of the conjugated character of a  $\pi$  system. Thus, the incorporation a photoisomerisable bridging ligand, dicyanonorbornadiene, in the structure of a  $\text{Ru}^{\text{II}}-\text{Ru}^{\text{III}}$  mixed-valence compounds was achieved in 1996.<sup>33</sup> After isomerization to a complex of quadricyclane, the intervalence band disappears. But the reverse transformation could not be obtained, due to the paucity of absorption bands in the quadricyclane spectrum.

A very attractive class of photochromic molecules has been presented by Irie since 1988.<sup>34</sup> They fulfil the traditional requirements for photochromism, *i.e.* stability, reversibility and separated absorption spectra. But in addition, their symmetrical structure and the presence of a delocalized  $\pi$  system in one of the forms, make them attractive candidates to constitute the bridging element between two redox centres. Thus, Lehn *et al.*

have described compounds where a dithienylperfluorocyclopentene moiety bridges pyridinium or phenol groups. Upon photoisomerization, several properties linked to electron delocalization, such as electrochemical response, non-linear optical activity, or fluorescence, are modified. But these effects do not correspond directly to a true electron transfer, but rather to the possibility for the molecule to respond to several stimulations, and even act as logic gates.

Associating reversible photochromism and intervalence electron transfer in the same molecule has been achieved for the first time quite recently.<sup>34</sup> We have prepared a complex in which dithienylperfluorocyclopentene bridges two cyclometallated species of the (bpy)<sub>2</sub>Ru(pp-) type. The starting form ("open") does not exhibit a detectable ruthenium–ruthenium electronic coupling, and thus constitutes the OFF state, in agreement with its non-conjugated structure. Photoisomerization, performed in the Ru<sup>II</sup>–Ru<sup>II</sup> state, yields the "closed" form, with the possibility of reversal by irradiation at a different wavelength. Finally, the "closed" form, once oxidized to the mixed-valence state, possesses a noticeable electronic coupling (0.025 eV), and thus represents the ON state, as could be anticipated from its conjugated electronic structure (Fig. 11). This demonstrates the possibility of truly locking or unlocking electron transfer on the molecular scale.

## 6 Conclusions and perspectives

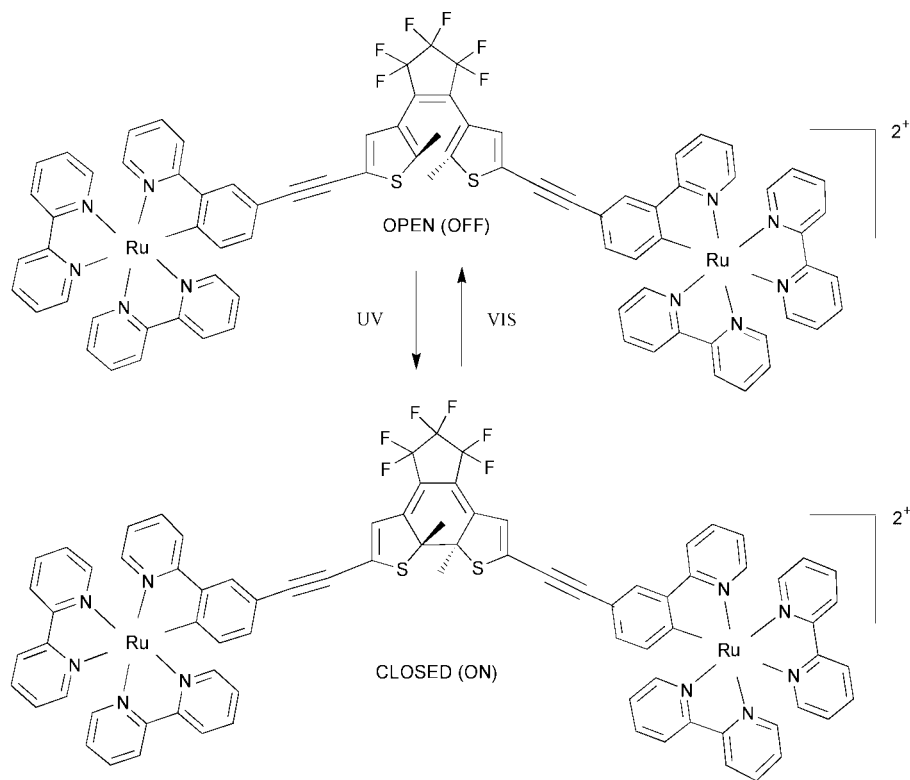
Intervalence transitions constitute a useful tool for monitoring intramolecular electron transfer and specifying the decay law of the interaction. For inorganic and organic compounds constituting series with various lengths, the rate of decay is well represented by an exponential law, with a  $\gamma$  factor varying in a surprisingly narrow range (0.08–0.12 Å<sup>-1</sup>). There also exist compounds with particularly strong couplings, but they are not generally members of series. The amount of accumulated data

now constitutes a precious guide for understanding the fundamental aspects of bridge-mediated electron transfer, and for devising efficient systems. The relation with electron transfer in biology has been recognised for many years. The recent development of nanosciences, particularly the measurements of an electrical current through metal–molecule–metal nanojunctions, constitutes another natural opening for these fundamental studies.

With intervalence transitions, it is possible to tackle challenging problems, such as the achievement of very strong couplings, and/or slow rates of decay with distance: properties that define molecular wires. An important result has been obtained, namely the demonstration of molecular switching (in the electrical sense of the term).

These transitions are however increasingly difficult to detect when the metal–metal distance approaches 20 Å, and it does not seem possible to exceed greatly this value. For longer systems exhibiting weaker intramolecular couplings, the recently described electrochemical method of Creager and Sumner offers a promising alternative.<sup>35</sup> It is based on the measurement by impedance spectroscopy of the electron transfer rate constant between a redox site and an electrode, across a linking unit embedded in a self-assembled monolayer. The roles of distance and topology can be addressed in a very similar way as for intervalence studies, showing the continuity of the methods.<sup>35</sup> This electrochemical experiment now constitutes a link between studies involving two monoatomic discrete metallic sites (molecular mixed-valence compounds), and those involving two bulk metals (metal–molecule–metal nanojunctions).

From a theoretical point of view, intervalence electron transfer still constitutes a challenge. One of the reasons is the difficulty in accurately computing the key parameter  $V_{ab}$ . It necessitates in particular the evaluation of small energy differences for molecules incorporating many difficulties: large size, open shell electronic structure, conjugated character prone to correlation effects, and finally a marked sensitivity to environment (solvent, counter ions). Disappointingly, *ab initio*



**Fig. 11** Photochemical switching of an intervalence transition in a cyclometallated complex using dithienylperfluorocyclopentene as spacer. Note that the photochemical transformations were performed on the Ru<sup>II</sup>–Ru<sup>II</sup> complex, while intervalence studies were performed on the Ru<sup>II</sup>–Ru<sup>III</sup> mixed-valence forms.<sup>34</sup>

methods have not really proved superior to cruder ones for the moment, and DFT methods are only in the infancy of their use. While waiting for improvements in the various methods, an apparently easier goal for the future could be the systematic theoretical determination of the nature (class II or III) of the mixed-valence compounds by geometry optimisation procedures.

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