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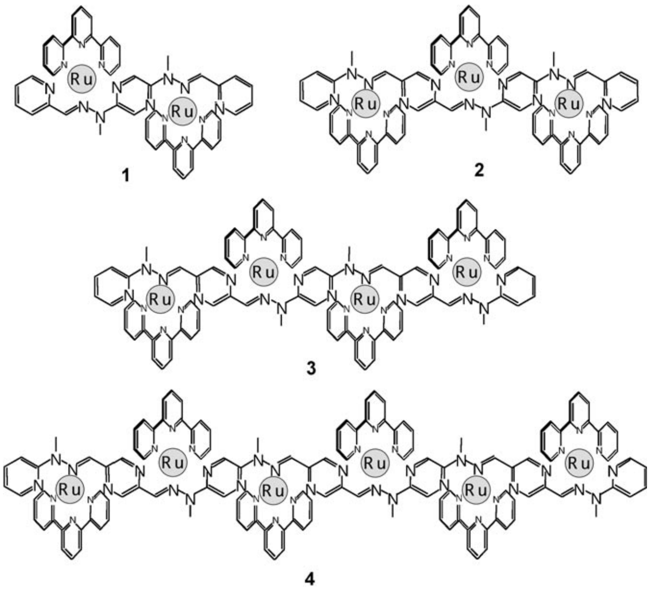
Molecular Wire Type Behavior of Polycationic Multinuclear Rack-Type Ru^{II} Complexes of Polytopic Hydrazone-Based Ligands**

Frédérique Loiseau, Francesco Nastasi, Adrian-Mihail Stadler, Sebastiano Campagna, and Jean-Marie Lehn**

Multicomponent supramolecular arrays based on metal-complex subunits are the focus of extensive investigation.[1] Among them, those involving Ru^{II} centers are highly attractive because of their photophysical and redox properties,[2] which make metallosupramolecular multicomponent Ru^{II} species ideal systems for the development of structurally organized, functionally integrated supramolecular units, which are of interest as photo- and/or redox-active molecular devices.[3] In particular, linear arrangements of Ru^{II} chromophores (rack systems[4]) have great potential to behave as "molecular wires".[5]

Broadly speaking, the term "molecular wire" identifies a roughly linear (supra)molecular assembly containing a molecular species ("spacer") which allows fast and efficient transfer of energy or charge between the peripheral subunits.[5,6] Without regard to the operating mechanism (superexchange-mediated or ohmic-type interaction[5a]), a key feature of a molecular wire is the dependence of the electronic coupling of peripheral sites on the distance.[6,7] Within accepted theories, such a dependence is expressed by the attenuation coupling parameter β.[5a,8]

Here we report new multinuclear ruthenium(II)–polypyridine rack-type complexes with two to six ruthenium centers (Scheme 1). These species are based on photo- and redox-active $\{Ru(tpy)^{2+}\}$ subunits (tpy = 2,2′:2′′,6′-terpyridine) appended to polytopic, molecular strands of increasing size that contain hydrazone-based terpy-type coordination centers. They can be viewed as made of two identical, peripheral subunits separated by zero (the dinuclear species, **1**), one (trinuclear, **2**), two (tetranuclear, **3**), and four (hexanuclear, **4**) roughly identical metal-containing spacer subunits. Details on the synthesis will be reported later (see also Ref. [4c]).



Scheme 1. Structural formulas of the studied compounds. Charges and counterions are omitted for clarity.

We note that the specific design of complexes **1**–**4** provides three main structural features of high significance for functional properties: 1) a linear array of Ru^{II} centers, as indicated by X-ray data,[4d] which results from 2) alternating positioning of the $\{Ru^{II}(terpy)\}$ units above and below the strand, and 3) efficient conjugation provided by the *para* location of the bridging nitrogen coordination sites of the pyrazine group.[4d]

Our results allow the evaluation for the first time (to the best of our knowledge) of the attenuation coupling parameter β within a series of multinuclear metal complexes from redox data.[9] It is also the first time that a β value has been obtained for metal-based, cationic spacer subunits.

All four complexes **1**–**4** exhibit multiple oxidation processes (Table 1, Figure 1). The first two oxidations can be attributed in all the cases to the two peripheral metal centers (see the Supporting Information), which occur at the same potential in the case of the hexanuclear species **4** (Table 1). In **3**, the third oxidation involves the inner subunit(s), as is the case for the second oxidation of **4**, whose differential pulse voltammogram also shows a third broad peak arising from overlapping unassigned processes.

The splitting of the oxidations of the peripheral metal centers in polynuclear, symmetrical metal complexes can be related to the electronic coupling between the sites.[10]

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[*] Dr. F. Loiseau, F. Nastasi, Prof. Dr. S. Campagna
Dipartimento di Chimica Inorganica
Chimica Analitica e Chimica Fisica
Università di Messina
Via Sperone 31, 98166 Messina (Italy)
Fax: (+39) 090-393-756
E-mail: campagna@unime.it

Dr. A.-M. Stadler, Prof. Dr. J.-M. Lehn
ISIS—Universite Louis Pasteur
8 Allee Gaspard Monge, BP 70028, 67083 Strasbourg cedex (France)
Fax: (+33) 390-245-140
E-mail: lehn@isis.u-strasbg.fr
Homepage: http://www-isis.u-strasbg.fr

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Table 1: Oxidation potentials of the studied compounds in argon-purged acetonitrile solutions.

Compound	$E(1/2)_{ox}$ [V versus SCE][a]
1	$+1.27$; $+1.52$
2	$+1.30$qr[b]; $+1.43$qr[b]
3	$+1.32$; $+1.37$; $+1.61$
4	$+1.34$[c]; $+1.43$; $+1.64$[d]

[a] Saturated calomel electrode. [b] qr = quasi-reversible [c] Bielectronic process. [d] Overlapping wave, probably comprising more than one electron (see text).

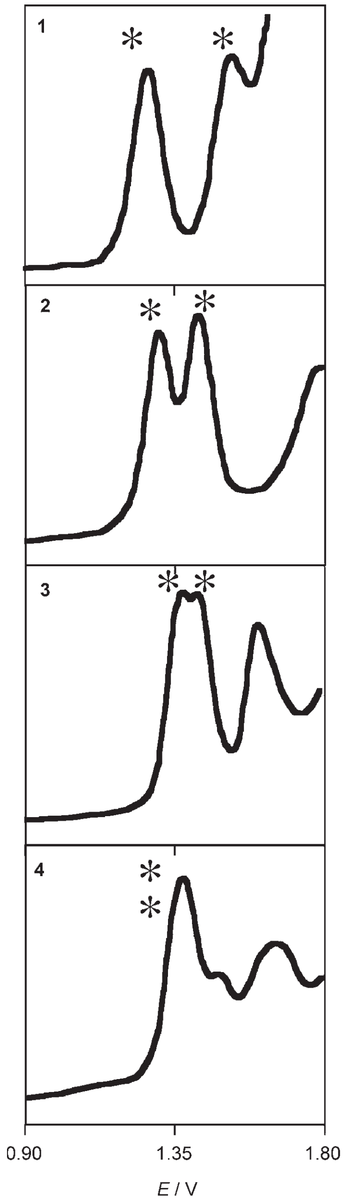

Figure 1. Differential pulse voltammograms of the studied compounds. Scan rate: 20 mVs^{-1}. The asterisks indicate the oxidation of the peripheral subunits.

However, whereas redox splitting is quite common for dinuclear systems,[2b,10,11] it is rare for systems of higher nuclearity, when interposed subunits are present. In fact, the oxidation processes of identical, peripheral metal centers in all the polynuclear Ru^{II} compounds with nuclearity higher than two reported in the literature occur at the same potential.[3b,12] Exceptions can be found in grids, which have a quite unusual structure,[1g,13] and in complexes containing particular tritopic ligands, such as hexaazatriphenylene (HAT) species.[14]

The results in Table 1 indicate that electronic interaction leading to sizeable redox splittings between the peripheral subunits occurs in the present rack complexes. It is the first time that a long-range electronic interaction across metal-based interposed units (up to a center-to-center distance of about 2 nm, as judged for **3**) could be determined by redox data.[15]

The splitting of the oxidation process of the peripheral units allows us to estimate the attenuation term β for electronic interaction within the series and therefore to have information on the ability of the mononuclear subunit(s) of this class of compounds to "conduct" electronically.[16] The β parameter is normally obtained for a series of modular spacers from electronic matrix elements H_{AB}. The H_{AB} values are calculated from electron-transfer rate constants or spectroscopic measurements, such as intervalence transfer bands,[10,17] according to Equation (1), where $H_{AB}(0)$ is the

$$H_{AB} = H_{AB}(0)\ \exp\left[(-\beta/2)\,(r_{AB}-r_0)\right] \tag{1}$$

value for the interaction at the "contact" distance r_0 (no interposed units; in our case, it would be the dinuclear system). It should be noted that Equation (1) is valid for calculations based on spectroscopic measurements. A slight modification is needed for H_{AB} values derived from electron-transfer rates.[5a,b]

Saturated spacers (such as bicyclooctane) have β values close to unity, and unsaturated spacers (for example, polyphenyls) have β values of about 0.5 $Å^{-1}$ or lower.[5a,18,19] The splitting of the ionization potentials gives satisfactory results as far as the H_{AB} calculation is concerned for polynorbornane dienes, and the results are comparable with H_{AB} values gained from alternative methods, including theoretical ones.[5a,20] Thus, the H_{AB} values in Equation (1) can be obtained from ionization potentials. Ionization potentials differ from oxidation potentials for several reasons, but to a first approximation one could assume that such differences would nevertheless allow there to be a direct proportionality between ionization and oxidation potentials. If so, the redox splitting can give an indication of electronic coupling (H_{AB}) between the sites.

Equation (2) can be formulated on the basis of the above assumptions, where $H'_{AB} = \Delta E/2$, ΔE corresponds to the oxidation splitting, and H'_{AB} would be proportional to H_{AB}.

$$H'_{AB} = H'_{AB}(0)\ \exp\left[(-\beta/2)\,(r_{AB}-r_0)\right] \tag{2}$$

A linear relationship between $\ln H'_{AB}$ and $(r_{AB}-r_0)$, with $-\beta/2$ as the slope, is found (Figure 2). Assuming r_{AB} (the edge-to-edge distance between peripheral sites) is equal to 0, 7, and 14 Å for **1**, **2**, and **3**, respectively (from model studies based on crystal data of dinuclear species related to **1**[4c]), a value of

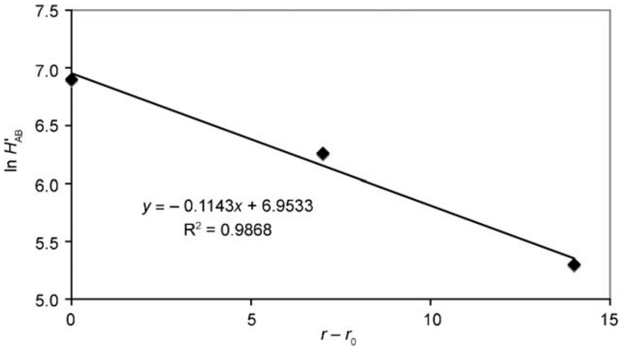

Figure 2. Distance dependence of H'_{AB}.

0.23 Å^{-1} is obtained for β. A splitting of the oxidation by 10 mV can be estimated for **4** from Figure 2: such a value is beyond detection by differential pulse voltammetry.

The calculated attenuation parameter β fits well with those of other spacers: it is smaller than those reported for most phenyl groups in organic systems (about 0.5 Å^{-1})[5a] and even smaller than those obtained from photoinduced energy-transfer rate constants between Ru^{II} and Os^{II} subunits separated by polyphenylene spacers (0.32 Å^{-1})[21] in mixed-metal dinuclear species and from spectroscopic measurements on olefin-bridged diruthenium and dialkylamino compounds (also 0.32 Å^{-1}).[22] Comparison with other metal-based "connectors" is not possible, as there are no literature data for similar species.

In conclusion, the low value of the attenuation parameter β obtained for the present linear multinuclear Ru^{II} complexes **1**, **2**, and **3** indicates that such rack-type arrays show properties typical of a genuine "molecular wire", and are thus of potential interest for implementation in supramolecular electronic devices.

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[6] Strictly speaking, molecular-wire behavior means electrical conduction through a bridge, which requires that the electron from the donor, which is thermally injected into the conduction band of the bridge, becomes localized within the bridge and is transported through the bridge, from donor to acceptor, by an incoherent scattering mechanism. For this type of system, the distance dependence of the electron transfer (and of the electronic coupling between the donor and acceptor) is ohmic, and therefore varies inversely with bridge length.[5,7] In the superexchange mechanism, the electron never resides on the bridge orbitals. However, the term "molecular wire" is commonly extended to systems operating through the superexchange mechanism as well, when electronic coupling between the peripheral active sites of the linear assembly is large enough to allow fast intercomponent electron- and/or energy-transfer processes.

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[15] Redox splitting is related in a straightforward manner to intercomponent electronic coupling only for weakly coupled systems, that is, when valence is vibrationally trapped (classes I and II of the Robin–Day mixed-valence systems).[10] Before discussing our data, it was necessary to clarify that our systems belong to this case. A detailed discussion on this point is contained in the Supporting Information.

[16] Redox splitting can also arise from a number of contributions (for example, electrostatic) besides electronic coupling.[10] Mean-

ingful β values can be obtained from redox splittings when those additional contributions are negligible. This is the case for the present systems.

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[19] Although β is usually considered a "bridge-specific" parameter, its value for a specific spacer (or spacer subunit) can vary on changing the peripheral subunits it connects. In fact the value of β depends on Δ, the energy gap between donor and bridge orbitals, and on T, the interaction between two adjacent, identical bridge subunits, according to the equation $\beta = 2\mathrm{In}\,|(\Delta/T)|$.[5a,8] While T can be considered invariant, Δ depends on the whole system, including the peripheral sites.

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