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Crossing the Boundaries

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"BLACK ABSORBERS" AND "FUZZY STEREOCHEMISTRIES"

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Preamble

An area of significant current research interest in inorganic chemistry is the rational design of supramolecular assemblies which may form the basis of new applicable materials. Photochemical molecular devices (PMDs), used in the conversion of light energy to chemical or electrical energy (i.e. artificial photosynthesis), light-activated molecular switches, etc. are an example of such an application.

In nature, the process of photosynthesis originates with light-promoted electronic excitation. In a series of short range, rapid electron-transfer steps, physically-separated reducing and oxidizing centres are created which have lifetimes sufficient that subsequent chemical reactivity may take place (the reduction of carbon dioxide to carbohydrates and the oxidation of water to oxygen, respectively).[1,2] Accordingly, any photosynthetic system - natural or artificial - must contain three essential components: *chromophores* at which light energy is absorbed, redox-active *quenchers* which allow the relay of the absorbed energy to the site of chemical reactivity, at which point *catalysts* promote the production of a high energy fuel. In the photobiological system, the relationship of these components is controlled by the three-dimensional enzyme matrix in which they are contained, and this (together with the trans-membrane nature of some of the relay processes) undoubtedly limits unwanted reaction pathways. In any artificial system such spatial considerations are unlikely to be any less important.

A key issue is the rapid physical separation of the excited electron from the chromophore, and the overall principle is represented below in Fig. 1, where a chromophore (**C**) is attached to redox-active groups. In the case where an electron donor (**D**) and an electron acceptor (**A**) are involved, the initial **D-C-A** species absorbs light energy and forms an excited state **D-*C-A**, which produces the redox charge-separated state **D$^+$-C-A$^-$** by a series of electron transfer steps.
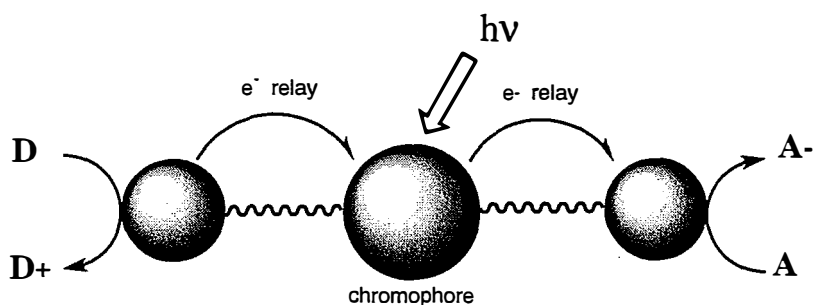

Figure 1.   Generalized principle of the process of charge separation.

As an exemplar of such studies, the work of Gust, Moore and coworkers is cited, where photoexcitation of a carotenoid-porphyrin-diquinone tetrad (represented $C-P-Q_A-Q_B$) gives rise to the charge-separated state $C^{\cdot+}-P-Q_A-Q_B^{\cdot-}$, rationalized via a series of electron transfers between adjacent groups.[3] In these particular studies, the components are actually mimics of the natural system - the porphyrin as the chromophore with the carotenoid and quinone moieties being donor- and acceptor-quencher functionalities, respectively.
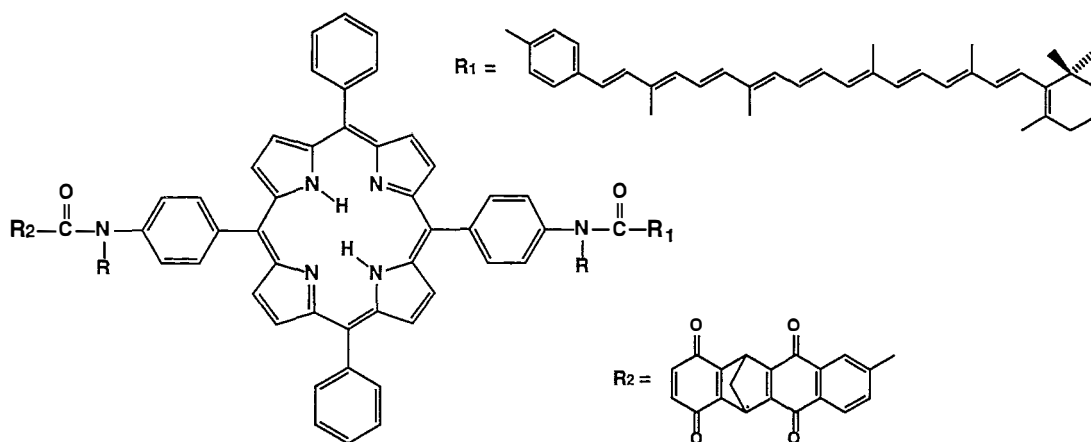
Figure 2. Chromophore-quencher tetrad C-P-Q_A-Q_B.[3]

Polymetallic molecules, appropriately constructed, could conceivably provide the basis for such a supramolecular system.[4,5] For the required building blocks, mononuclear transition metal complexes of the d^6 metal centres ruthenium(II), osmium(II) and rhenium(I) with polypyridyl ligands {e.g. bpy = 2,2'-bipyridine and phen = 1,10-phenanthroline and their analogues} are of particular interest as precursors because of their extensive (and well studied!) photochemistry.[6] Of these, the ruthenium compounds have received most attention, as the synthetic versatility of osmium is comparatively limited and rhenium species tend to lack broad-band absorption in the visible spectral region. The capacity for variation of the photophysical, spectral and redox characteristics by ligand control is extensive, and this has been well documented for homoleptic and bis(heteroleptic) complexes of ruthenium(II) with bidentate polypyridyl ligands.[7,8]

In this presentation, I wish to look briefly at the aspects of our recent work, firstly on the deliberate control of the chromophoric and redox properties of metal centres which are to be used as components of polymetallic supramolecular assemblies, and secondly on the control of stereochemistry (and therefore the spatial relationship of the component metal centres) within such assemblies.
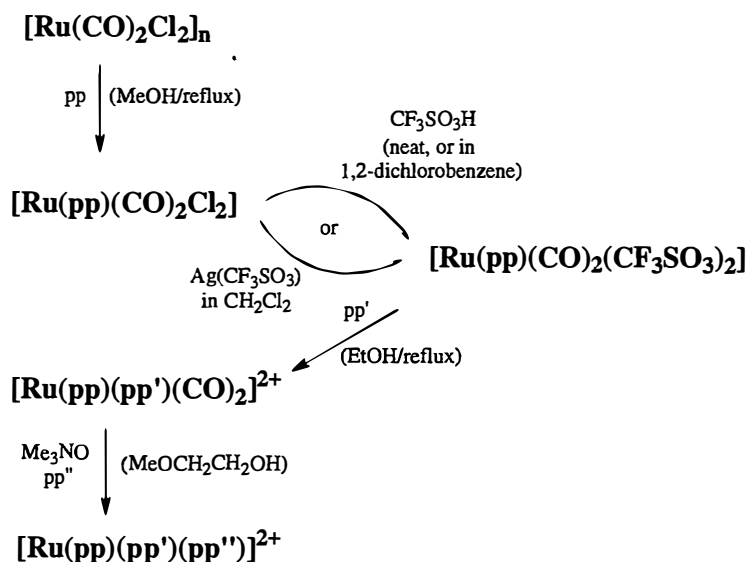
"Black Absorbers".

The simplified MO diagram of a d^6 metal centre with N-heterocyclic ligands is shown in Fig.3.
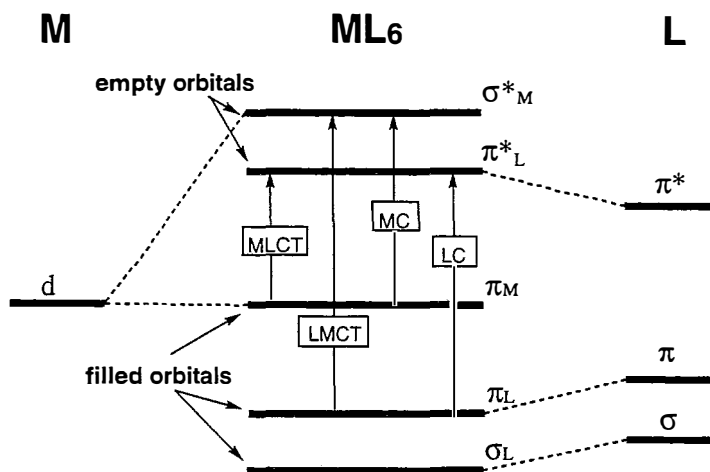
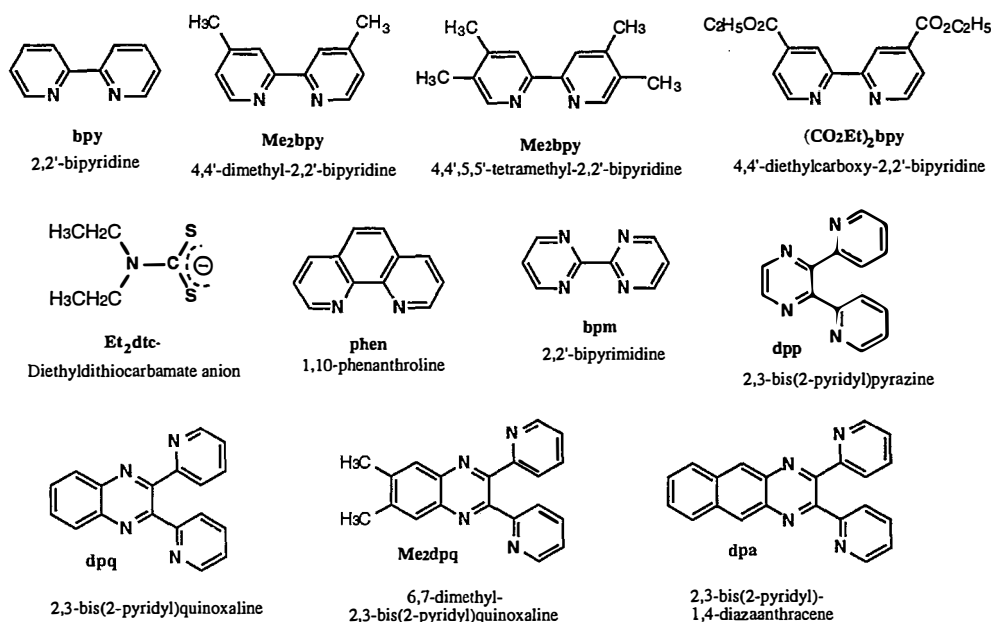**Figure 3.** Simplified MO diagram for ML_6 species.

The lowest energy transition will be from the filled metal-based $d\pi$ level to the lowest unoccupied ligand-based π^* orbital (i.e. metal-to-ligand charge transfer or MLCT). Modification of the absorbance may be achieved by variation of either of the $d\pi$ or the π^* levels, which rely on the ability to control the ligand environment of the metal centre.

We have recently developed synthetic methodologies for heteroleptic tris(bidentate) complexes of Ru(II) and Os(II).[7,9] In the ruthenium case, the technique is based on the sequential addition of the polypyridyl ligands to the oligomeric precursor $[Ru(CO)_2Cl_2]_n$, as summarized in Fig. 4.

$[Ru(CO)_2Cl_2]_n$

pp | (MeOH/reflux)

$[Ru(pp)(CO)_2Cl_2]$

CF$_3$SO$_3$H
(neat, or in
1,2-dichlorobenzene)

or

Ag(CF$_3$SO$_3$)
in CH$_2$Cl$_2$

$[Ru(pp)(CO)_2(CF_3SO_3)_2]$

pp'
(EtOH/reflux)

$[Ru(pp)(pp')(CO)_2]^{2+}$

Me$_3$NO
pp" | (MeOCH$_2$CH$_2$OH)

$[Ru(pp)(pp')(pp")]^{2+}$

Figure 4. Synthetic scheme for heteroleptic tris(bidentate) complexes of Ru(II)

A very wide range of complexes has been produced, and the effect of the ligand variation on the metal $d\pi$ and ligand π^* levels probed. The π^* level will lowered by the presence more easily reducible ligands - e.g. those with electron-withdrawing substituents (e.g. (EtCO$_2$)$_2$bpy cf. bpy) and raised by the use of electron-donating substituents (e.g. Me$_2$bpy cf. bpy). The $d\pi$ level will be raised by the attachment of ligands which are electron rich and promote π-donation to the metal (e.g. dithiocarbamate or thiocyanate ions).

bpy
2,2'-bipyridine

Me$_2$bpy
4,4'-dimethyl-2,2'-bipyridine

Me$_2$bpy
4,4',5,5'-tetramethyl-2,2'-bipyridine

(CO$_2$Et)$_2$bpy
4,4'-diethylcarboxy-2,2'-bipyridine

Et$_2$dtc-
Diethyldithiocarbamate anion

phen
1,10-phenanthroline

bpm
2,2'-bipyrimidine

dpp
2,3-bis(2-pyridyl)pyrazine

dpq
2,3-bis(2-pyridyl)quinoxaline

Me$_2$dpq
6,7-dimethyl-
2,3-bis(2-pyridyl)quinoxaline

dpa
2,3-bis(2-pyridyl)-
1,4-diazaanthracene

From the MO diagram in Fig. 3, it can be seen that in a homoleptic complex (where the three pp ligands are identical), the π^* levels are essentially degenerate. By variation of the π^* levels in the heteroleptic complex, the π^* levels will differ and the various absorptions can be moved by design and appropriate choice of ligand (Fig. 5).

Homoleptic species ("O_h")   Heteroleptic species ("O_h")
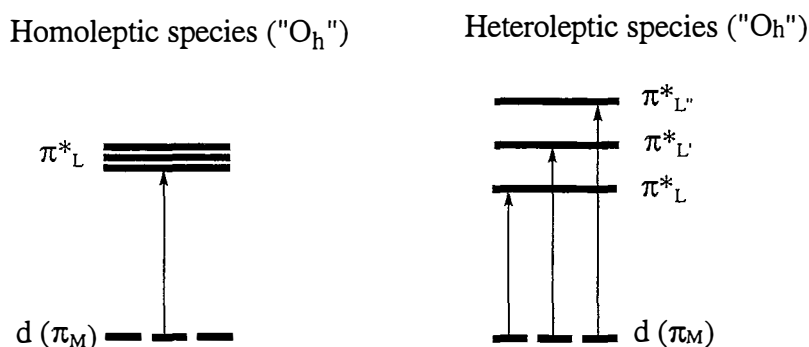
Figure 5. $d\pi \rightarrow \pi^*$ transitions in homo- and hetero-leptic tris(bidentate) species.

Three examples are given below to illustrate the point. In Fig. 6A are shown the spectra of the series of complexes $[Ru(Me_2bpy)(Me_4bpy)(pp)]^{2+}$ where pp are the series of ligands dpp, dpq and dpa (for which the π^* levels decrease with increasing delocalization). A corresponding red shift of the lowest energy MLCT absorption is observed in the visible spectrum, but with the creation of a "gap" in the region of the spectrum between 400-500 nm. By replacing the Me$_4$bpy ligand with $(EtCO_2)_2bpy$ (which has a lower π^* level), this gap can essentially be filled, and the series of complexes $[Ru(Me_2bpy)\{(EtCO_2)_2bpy\}(pp)]^{2+}$ (Fig. 6B) show the same trend as before, but have significant absorbance (i.e. $\varepsilon > 10,000\ M^{-1}cm^{-1}$) over the entire visible spectrum. In other words they are essentially "black absorbers".

The effect of inclusion of a ligand such as Et_2dtc^-, which is a strongly π-donating ligand and raises the $d\pi$ level of the metal, can be seen in Fig. 6C, where the absorbance is even further red-shifted.
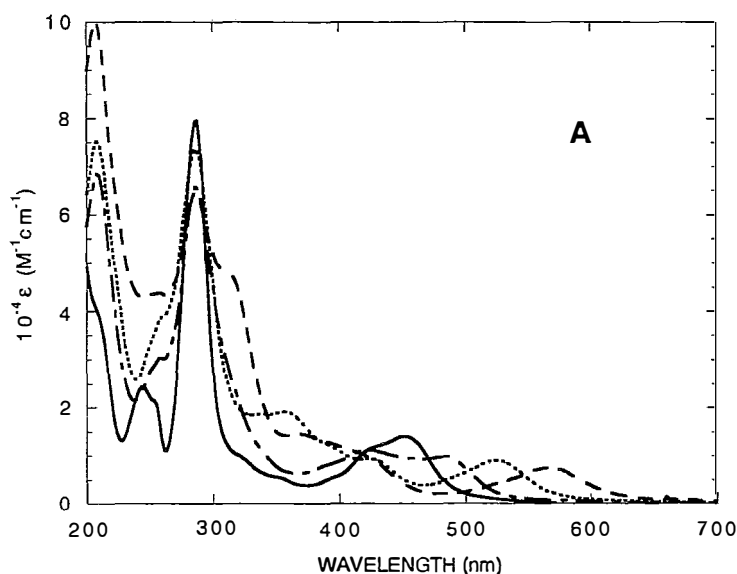
Figure 6.   (A) Electronic spectra (acetonitrile solution) of $[Ru(bpy)_3]^{2+}$ (————), and $[Ru(Me_2bpy))(Me_4bpy)(L)]^{2+}$ {where L = dpp (—— – —— –) , dpq (- - - - - -) and dpa (— — — —)}.

(B)   [Ru(bpy)$_3$]$^{2+}$ (———) and [Ru(Me$_2$bpy){(EtCO$_2$)$_2$-bpy}(L)]$^{2+}$ {where
       L = dpp (—— – —— –) , dpq (- - - - - -) and dpa (— — — —)}.
(C)   [Ru(bpy)$_3$]$^{2+}$ (———), [Ru(Me$_2$bpy)(Me$_4$bpy)(dpa)]$^{2+}$
       (— — — —), and [Ru(Me$_2$bpy){(EtCO$_2$)$_2$-bpy}(dpa)]$^{2+}$ (- - - - - -).
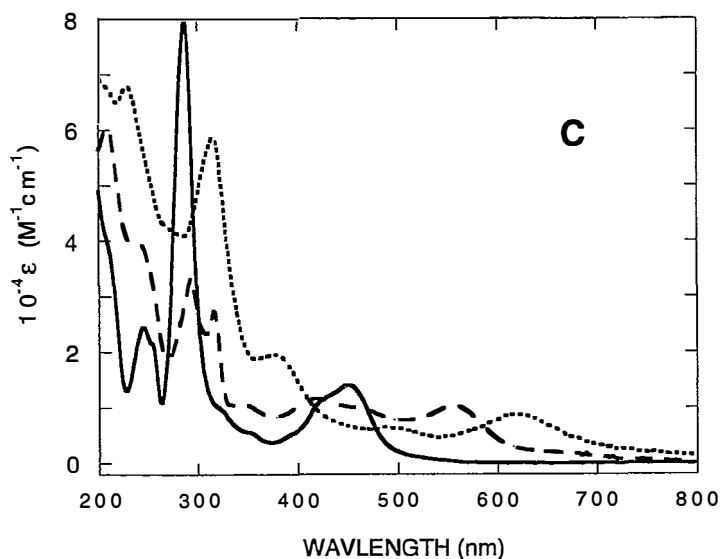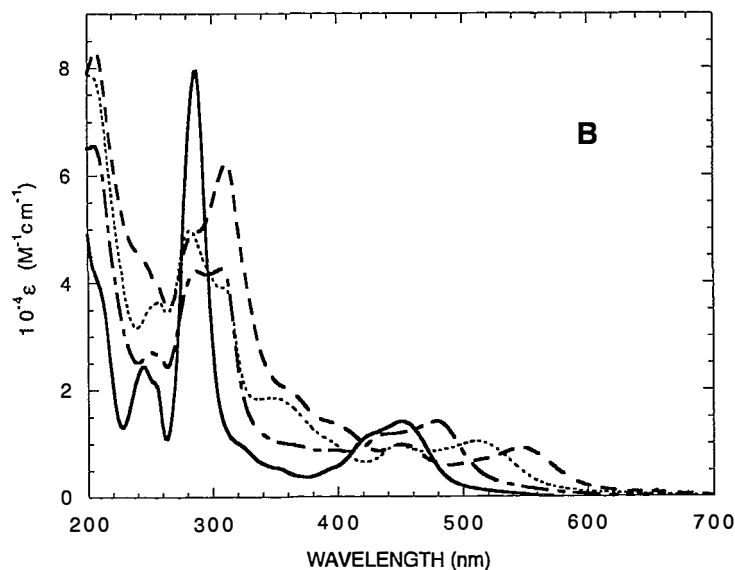
It is also apparent from the MO diagram in Fig. 3 that reduction places the electron in the LUMO, which is the π^* level of the ligand. Accordingly, the reduction processes provide a technique of "mapping" the π^* levels within each complex. A perusal of the redox couples of a selected series of complexes in Table 1 will illustrate the point. In a homoleptic complex such as [Ru(bpy)$_3$]$^{2+}$, the progressive reduction of the three ligands takes place at more cathodic potentials - as may be anticipated as the overall positive charge on the complex decreases. As the bpy ligands are replaced by other ligands, there is a clear pattern that the first reduction mirrors the π^* level of the most easily reduced ligand and subsequent redox potentials are consistent with values associated with the ligand involved experiencing the second or third reduction in a homoleptic complex containing it.

Lever and coworkers have recently proposed a system of parametrization of oxidation[10] and reduction potentials[11] in metal complexes, based on a ligand parameter E_L. The relationship is given by eq. 1, where S_M and I_M are constants for a particular metal, and the E_L parameter for each ligand is derived from the same equation using the homoleptic complex of ruthenium(II).

$$E_{calc} = S_M \sum E_L(L) + I_M \qquad \ldots (1)$$

For the first ligand-based reduction process, there is a similar relationship

$$E_{red} = S_L \sum E_L(L) + I_L \qquad \ldots (2)$$

An implication of the use of the paramter $E_L(L)$ in these contexts is that ligand behaviour is independent of the identity of the metal centre, and also of the same metal centre in circumstances where the other ligands may be widely varied in terms of their σ-donor and π-donor/acceptor characteristics. The present electrochemical study of the heteroleptic species constitutes a major test of this proposal, and it shows the parametrization to be remarkably successful in a predictive sense. In one case, $viz.$ [Ru(Me$_2$bpy)(dpp){(EtCO$_2$)$_2$bpy}]$^{2+}$, where there is some ambiguity in the choice of the either dpp or (EtCO$_2$)$_2$bpy as the ligand possessing the lower π^* level, a study of the reduction potentials and eq. 2 clearly identifies dpp as the lower, which is important in the study of the spectroscopy and photophysics.

Complex	Oxidation Ru III/II	Reduction Ligand Reductions		
[Ru(bpy)$_3$]$^{2+}$	+1.29	-1.33	-1.52	-1.78
[Ru(bpy)(Me$_2$bpy*)(5-Me-phen†)]$^{2+}$	+1.24	-1.37	-1.56†	-1.81*
[Ru(bpy)(Me$_2$bpy*)(bpm#)]$^{2+}$	+1.37	-1.03#	-1.49	-1.74*
[Ru(bpy)(Me$_2$bpy*){(CO$_2$Et)$_2$bpy‡}]$^{2+}$	+1.35	-1.01‡	-1.48	-1.69*
[Ru(Me$_2$bpy*)(Me$_4$bpy#)(dpp§)]$^{2+}$	+1.26	-1.09§	-1.61*	-1.98#
[Ru(Me$_2$bpy*){(CO$_2$Et)$_2$bpy‡}(dpp§)]$^{2+}$	+1.45	-0.96§	-1.19‡	-1.66*
[Ru(Me$_2$bpy*){(CO$_2$Et)$_2$bpy‡}(Me$_2$dpq§)]$^{2+}$	+1.44	-0.83§	-1.12‡	-1.64*
[Ru(Me$_2$bpy*){(CO$_2$Et)$_2$bpy‡}(dpq§)]$^{2+}$	+1.47	-0.75§	-1.12‡	-1.62*
[Ru(Me$_2$bpy*){(CO$_2$Et)$_2$bpy‡}(dpa§)]$^{2+}$	+1.47	-0.59§	-1.09‡	-1.47*
[Ru(Me$_2$bpy*){(CO$_2$Et)$_2$bpy‡}(Et$_2$dtc)]$^+$	+0.62	-1.25‡	-1.45*	
[Ru{(CO$_2$Et)$_2$bpy‡}(dpa§)(Et$_2$dtc)]$^+$	+0.79	-0.76§	-1.23‡	-1.73§

Table 1. Redox couples for a selection of tris(bidentate) complexes of polypyridyl complexes of ruthenium {ligand annotations refer to potentials listed for that complex only)

"Fuzzy Stereochemistries".

As was intimated earlier, polymetallic ligand-bridged assemblies are of particular interest in the design of artificial materials for photochemical molecular devices, because of the possibility of variation of the chromophoric, redox and catalytic characteristics of the metal components. The previous section attests to the versatility in the first two categories. In the design of such supramolecular assemblies, the particular use of tris(bidentate) moieties as the "building blocks" is necessary to exploit such variation.

One example of a large number of ligand-bridged polynuclear assemblies based on this motif is a decanuclear species (shown in Fig. 7), which has been synthesized in homo- or hetero-metallic forms containing Ru(II) and/or Os(II).[12] The bridging ligand is 2,3-bis(2-pyridyl)pyrazine (dpp) and terminal ligands 2,2-bipyridine (bpy). From photophysical studies it demonstrates that energy transfer may be directed from a number of peripheral sites (M_p) to a single central site (M_c), whereas in other cases energy is transferred in the opposite direction.


Terminal ligand: ▬

2,2'-bipyridine (bpy)

Bridging ligand

2,3-bis(2-pyridyl)pyrazine (2,3-dpp)

● = Mp   ◐ = Mc
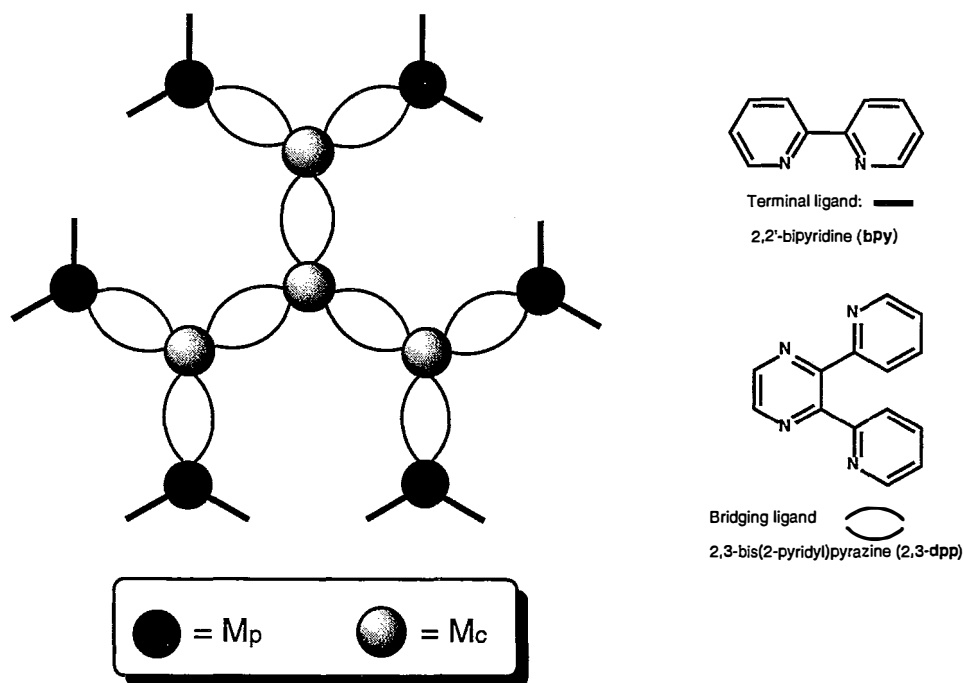
Figure 7. The decanuclear species $[Ru_{10}(dpp)_9(bpy)_{12}]^{20+}$.[12]

In such an assembly, since the internal metal centres (M_c) are $[Ru(dpp)_3]^{2+}$ moieties, they all can exhibit *mer/fac* geometrical isomerism as dpp in non-symmetrical. In addition, all ten metal centres may be chiral. As a result of this, there are in fact 6,144 diastereoisomers of this species - each with an enantiomeric form! While it is unlikely that all these stereoisomers would be represented in a synthesized mixture, it emphasizes the point that the stereochemistry of such systems is very complicated. Furthermore, the presence of a plethora of stereoisomers complicates the characterization of the complex by techniques such as NMR, the interpretation of which is rendered extremely difficult as the diastereoisomeric complexes have non-equivalent NMR spectra. It also implies that the electrochemical and photophysical data measured represent an average of the various forms.

As another example, a study was presented by Brewer and coworkers on the electrochemical and photophysical properties of the trinuclear species $[\{Ru(bpy)_2\}_2\{Os(dpp)_2Cl_2\}]^{4+}$.[13] In this complex the bridging Os centre may adopt a *cis(Cl)* or *trans(Cl)* geometry, and since the dpp ligand is non-symmetrical, the *cis(Cl)* form has three geometric isomers and the *trans* isomer two. All the *cis* isomers may have chiral forms, as may both ruthenium centres. As a result, there are actually sixteen possible diastereoisomers, all but two of which have enantiomeric forms. Of course, the full complement may not necessarily exist. However, in the representations in Fig. 8, the stereochemistry in such a linear trinuclear species may be very different for a relatively small change - the species shown are both Δ(Ru)Δ(Os)Δ(Ru) forms, and differ only in that the geometric arrangement about the Os center is *cis(Cl)/cis(pyrazine)* and *cis(Cl)/trans(pyrazine),* shown below as **A** and **B** respectively. The consequences on the relative disposition of the two "terminal" ruthenium centres is quite profound.

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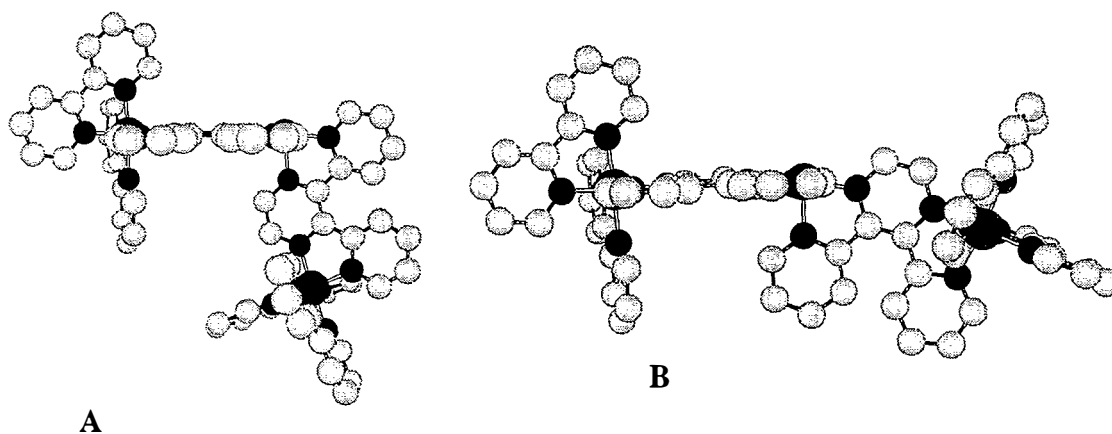
Figure 8. Two diastereoisomers of [{Ru(bpy)$_2$}$_2${Os(dpp)$_2$Cl$_2$]$^{4+}$ (H atoms omitted).[13]

It is clear that in many of the systems studied, the stereochemical identity of the products is far from clear: a situation called *"fuzzy stereochemistry"* by von Zelewsky.[14] Structural control within such polymetallic molecules is paramount since the type and arrangement of metal centres greatly influences energy migration patterns. But despite an extensive and rapidly growing literature on the synthesis and electronic characteristics of such compounds,[15] the issue of the effects of stereoisomerism on those properties, while receiving occasional tacit acknowledgment, has rarely been addressed. An understanding of such aspects seems fundamental: photo-promoted intramolecular electron or energy transfer between chromophoric and catalytic sites are essential processes in artificial assemblies designed as photochemical molecular devices, and they will be spatially dependent. The assembly is required to provide the molecular framework which is a feature associated with the enzyme matrix in natural systems, and which controls the directional qualities of the transfer processes.

Our synthetic methodology, discussed above (Fig. 4), may be extended to polynuclear species by the use of a "complexes as ligands" technique, and we have been able to show that the final step proceeds with retention of stereochemical integrity.[16,17] Coupled with our development of a chromatographic technique that allows separation of stereoisomers of mono- and oligo-nuclear complexes of this type, we are in position to synthesize individual isomers of the polynuclear assemblies. The general concept is summarized in Fig. 9, but the extension of that principle and its significance may be easily inferred.

Λ-(+)-[Ru(phen)$_2$(CO)$_2$]$^{2+}$
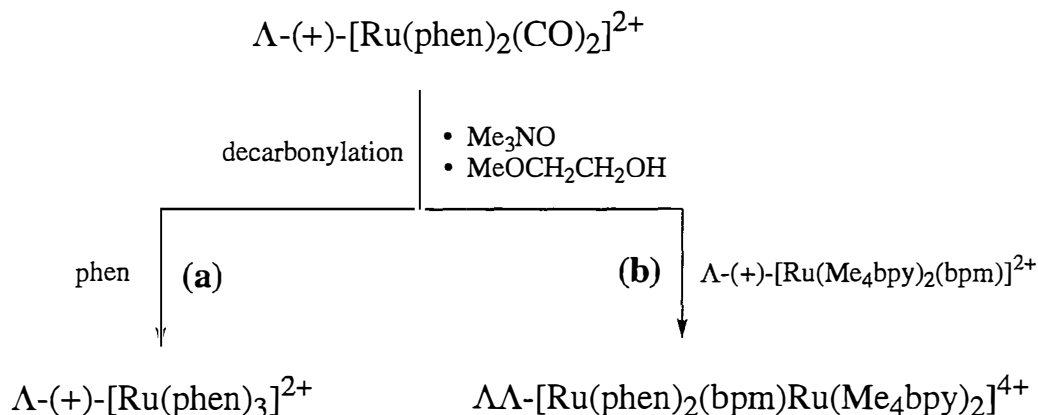
Figure 9. Stereochemical course of decarbonylation reactions.[17]

But one may pose the question of whether such stereochemical niceties are actually important in the larger picture of intramolecular electron and energy transfer processes. In the simplest case of a dinuclear ligand-bridged complex with a symmetrical bridge (e.g. bpm = 2,2'-bipyrimidine) and two metal centres with the same coordination environment {e.g. $Ru(bpy)_2^{2+}$}, there are two diastereoisomers, shown in Fig. 10.

meso {ΔΛ}   *rac* {ΔΔ ≡ ΛΛ}
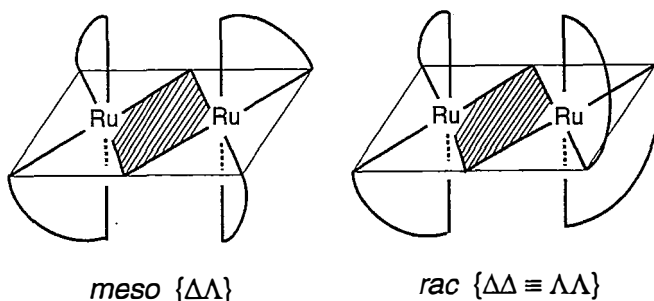
Figure 10. Schematic representation of the diastereoisomeric forms of the dinuclear ligand-bridged species [{Ru(pp)₂}₂(BL)]⁴⁺.

There is a significant difference between the *rac* and *meso* diastereoisomers. The terminal polypyridyl ligands "above" and "below" the plane of the bridging ligand bear a significantly different relationship, as the terminal polypyridyl ligands "above" and "below" the plane of the bridging ligand are approximately parallel in the ΔΔ/ΛΛ form, whereas they are perpendicular in the ΔΛ/ΛΔ stereoisomer. This is shown in a schematic manner in Fig. 10.

R = H: azobis(2-pyridine) {apy}

= CH₃: azobis(4-methyl-2-pyridine) {mapy}

(ΔΛ)   (ΔΔ)
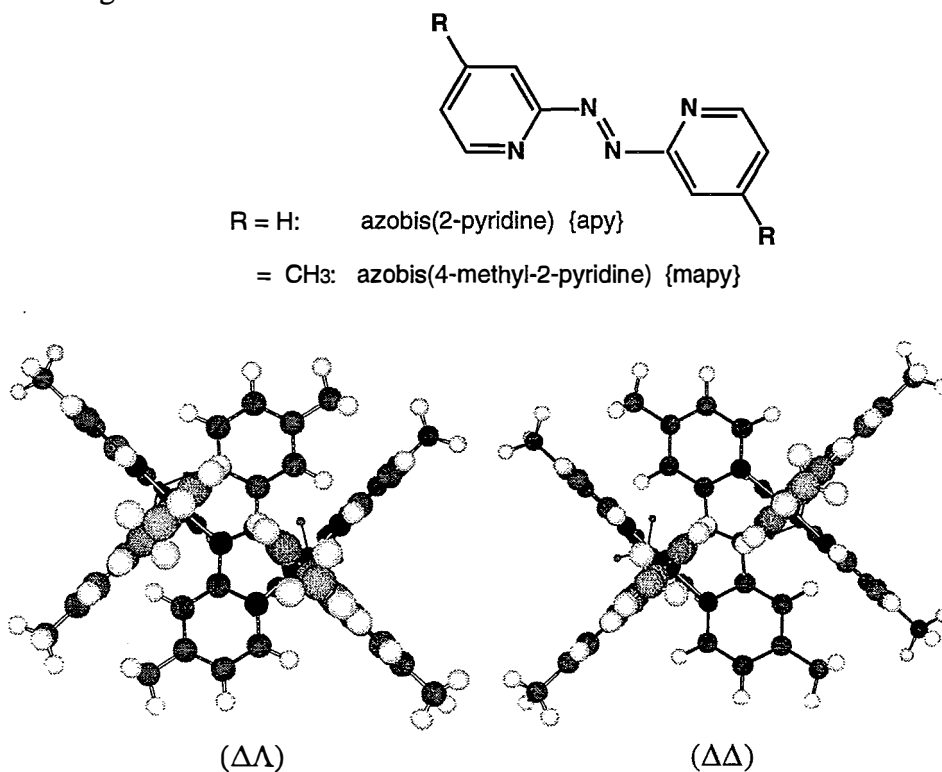
Figure 11. CHEM 3D™ representations of the diastereoisomeric forms of [{Ru(Me₂bpy)₂}₂(μ-mapy)]⁴⁺.

To probe the stereochemical effects in dinuclear species, we chose to investigate the series of complexes [(pp)₂Ru(BL)Ru(pp')₂]²⁺, where pp/pp' were the terminal ligands

bpy or Me_2bpy, and the bridging ligand BL was of the α-azodiimine type (apy or mapy).[18] Ligands possessing the azo functionality have extremely low-lying π^* orbitals and exhibit a very high degree of metal-metal interaction.[19,20] Bridging ligands of this type also are found to enhance the structural differences between the diastereoisomers of such dinuclear species (Fig. 11).[18]

Electrochemical studies may be used to map the location of the reduction processes. In earlier work on these species, it was assumed that the first four reductions were based on the azo-type ligand.[20] A comparison of the differential pulse polarograms of the reductions of the $[(bpy)_2Ru(Me_2apy)Ru(bpy)_2]^{2+}$, $[(Me_2apy)_2Ru(Me_2apy)Ru(Me_2apy)_2]^{2+}$ and $[(bpy)_2Ru(Me_2apy)Ru(Me_2apy)_2]^{2+}$ in Fig. 12 show quite clearly that the third reduction is isolated on the terminal ligands, and they are split in the "un-symmetical" dimer.
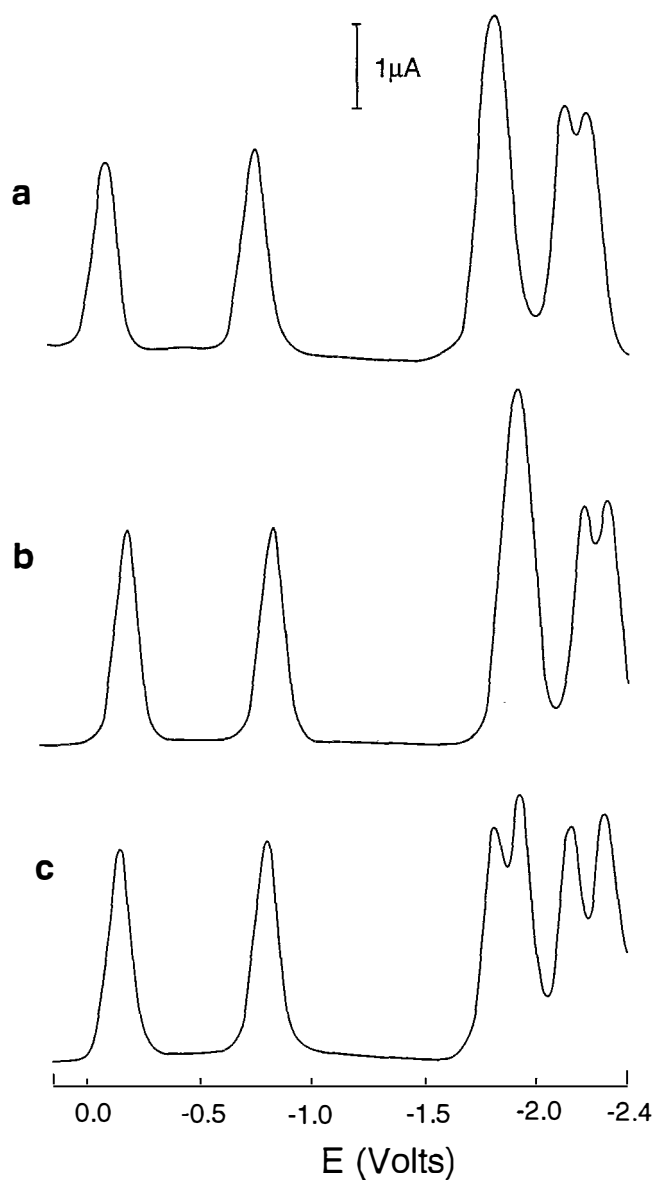

Figure 12. Differential pulse voltammograms for the *rac* $(\Delta\Delta/\Lambda\Lambda)$ forms of (a) $[\{Ru(bpy)_2\}_2(\mu\text{-mapy})]^{4+}$, (b) $[\{Ru(Me_2bpy)_2\}_2(\mu\text{-mapy})]^{4+}$, and (c) $[(bpy)_2Ru(\mu\text{-mapy})Ru(Me_2bpy)_2]^{4+}$ $(CH_3CN/0.1M\ [(n\text{-}C_4H_9)_4]ClO_4$ solution; Pt working electrode; Ag/Ag^+ reference electrode).

The diastereoisomers show differences in their physical characteristics, even in their visible absorption spectra (Fig. 13).
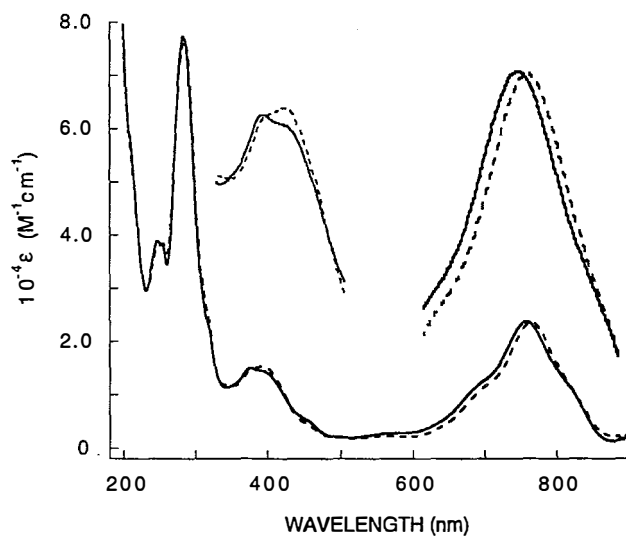

Figure 13. UV-visible absorption spectra (CH₃CN solution) of *meso-* (————) and *rac* (- - - -) [{Ru(bpy)₂}₂(μ-apy)](PF₆)₄.

And their electrochemical properties are different. This is actually more easily seen in a related system [{Ru(bpy)₂}₂(μ-dpa)]²⁺ {dpa = 2,3-bis(2-pyridyl)-1,4-diaazaanthracene}. In the case of oxidation of the two Ru(II) centres to Ru(III), if the two metal centres are insulated from one another by the bridge, then the two oxidation processes will take place independently at the same potential. On the other hand, if there is communication between the two metal centres across the bridge, the two oxidation processes will occur at different potentials as the second oxidation is affected by the first process. The greater the communication, the greater the separation of the two redox couples.


dpa
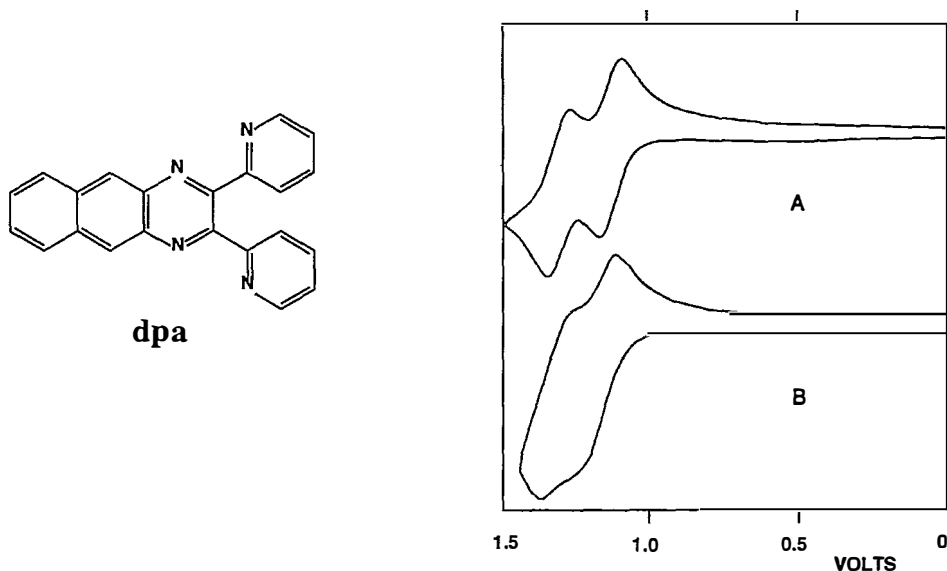
Figure 14. Cyclic voltammetry of [{(bpy)₂Ru}₂(μ-dpa)]⁴⁺ (CH₃CN/0.1M [(n-C₄H₉)₄]ClO₄ solution; vs. Ag/Ag+).[21]

Clearly, the separation between the potentials of the two diastereoisomers is greater for the form in Fig. 14A, which is the diastereoisomer in which the terminal rings on either side of the bridge are parallel. To our knowledge, this is the first direct observation within a ligand-bridged dinuclear species of such differences in the communication induced by the stereochemistry .
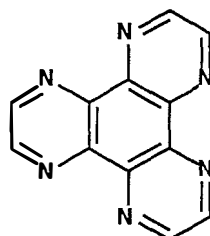
Such examples may be extended to higher nucleates: in dinuclear (Fig. 15) and trinuclear (Fig. 16) complexes involving the bridging ligand HAT (1,4,5,8,9,12-hexaazatriphenylene; shown above), we have separated the diastereoisomers by a combination of our synthetic and chromatographic techniques. Again, the differences between the diastereoisomers in terms of the relative orientations of the terminal ligands are obvious.
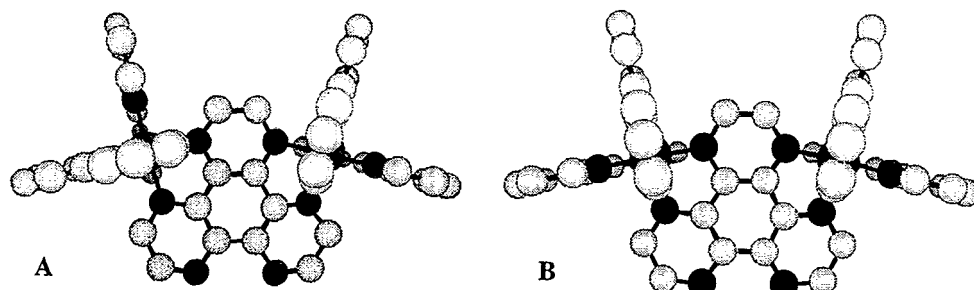
Figure 15. Chem 3D™ representation of diastereoisomeric forms of [{Ru(bpy)$_2$}$_2$(μ-HAT)]$^{4+}$: (A) *rac* {ΔΔ (≡ ΛΛ)}; (B) *meso* {ΛΔ}. Hydrogen atoms are omitted for clarity.
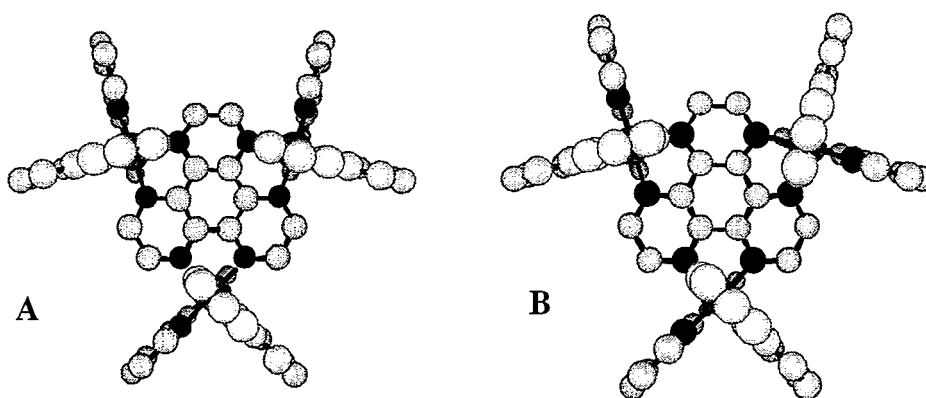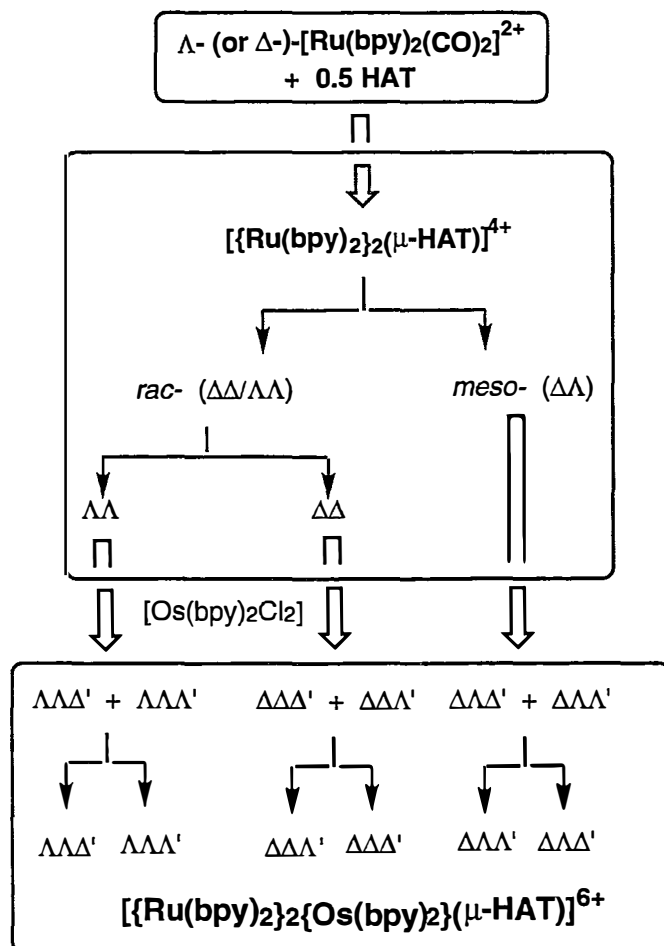

Figure 16. Chem 3D™ representation of diastereoisomeric forms of [{Ru(bpy)$_2$}$_3$(μ-HAT)]$^{6+}$: (A) Heterochiral {ΔΔΛ}; (B) Homochiral {ΔΔΔ (≡ ΛΛΛ)}. Hydrogen atoms are omitted for clarity.

The electronic absorption and electrochemical properties of the diastereoisomers in both series are virtually indistinguishable, but photophysical studies indicate differences between the forms. Again, this emphasizes that stereochemistry will play a part in

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determining the nature of the communication between the stereoisomers in these and larger assemblies.

We have in fact isolated all the stereoisomers of the heterometallic trinuclear complex (Fig. 17), and the comparative study of the characteristics of these species is in progress.[22]

Λ- (or Δ-)-[Ru(bpy)$_2$(CO)$_2$]$^{2+}$
+ 0.5 HAT

∏

⇩

[{Ru(bpy)$_2$}$_2$(μ-HAT)]$^{4+}$

rac- (ΔΔ/ΛΛ)   meso- (ΔΛ)

ΛΛ   ΔΔ
∏   ∏

⇩ [Os(bpy)$_2$Cl$_2$] ⇩   ⇩

ΛΛΔ' + ΛΛΛ'   ΔΔΛ' + ΔΔΔ'   ΔΛΔ' + ΔΛΛ'

ΛΛΔ'   ΛΛΛ'   ΔΔΛ'   ΔΔΔ'   ΔΛΔ'   ΔΛΛ'

[{Ru(bpy)$_2$}$_2${Os(bpy)$_2$}(μ-HAT)]$^{6+}$

Figure 17. Scheme for the isolation of the stereoisomers of [{Ru(bpy)$_2$}$_2${Os(bpy)$_2$}(μ-HAT}]$^{6+}$: chromatographic procedures are indicated by single arrows, synthetic procedures by double arrows).[22]

In instances where the physical properties of mixtures of isomers of mononuclear and oligonuclear systems have been investigated, there have been numerous assertions that stereochemistry will have little influence on electronic transitions and intramolecular electron and energy transfer processes. From our studies reported here, it is apparent this is not the case. And it would be the normal expectation such variations would become more significant as the size of the assembly increased: we are currently investigating oligomers of higher nuclearity to clarify this issue.

This paper serves to emphasize the importance of electrochemical techniques in these studies. Firstly, they have provided information on redox characteristics, and allowed a mapping of the ligand * levels involved in mono- and oligo-nuclear complexes. In addition, for the oligonuclear species they have provided information on the intermetal communication in such species, and allowed investigations of the intervalence character of some of these processes. It is envisaged that a combination of electrochemical and spectral studies will continue to provide further insight in intramolecular transfer processes in such systems.

Acknowledgments

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