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# Inter-chromophore electronic interactions in ligand-bridged polynuclear complexes: a comparative study of various bridging ligands

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## Abstract

A brief survey of various bridging ligands that are currently available for the synthesis of light harvesting systems and of the principles of analysis of electronic coupling is followed by a comparative analysis on what is known on the role of bridging ligands in modulating the electronic communication between the chromophores. Polynuclear complexes of the type $[(LL)_2M_1-(BL_1)-M_2(LL')_2]^{n+}$ and $[(X)(LL)_2M_1-(BL_2)-M_2(LL')_2-(BL_2)-M_3(LL'')_2(X)]^{n+}$, where LL, LL', LL'' refer to bipyridine-type ligands (or non-chromophoric ones such as –Cl, $H_2O$, –CN, CO, ...); $BL_1$ represent bis-bidentate type bridging ligands such as dpp or BPBT and $BL_2$ represent bis-monodentate such as cyanide; $M_1$, $M_2$ and $M_3$ stand for the metal centres Ru(II), Os(II) and Re(I), are considered.

*Keywords:* Electronic interactions; Ruthenium complexes; Osmium complexes; Polynuclear complexes

## 1. Introduction

For a number of years we have been studying sensitization of wide bandgap semiconductor $TiO_2$ using inorganic metal complexes [1]. The majority of the work used polypyridine complexes of transition metal ions as sensitizers, since a lot is known on the CT excited state and their electron/energy transfer reactions [2]. The CT transitions of these complexes are moderately intense ($\epsilon \geqslant 10\,000$ $M^{-1}$ $cm^{-1}$), but in a given mononuclear complex, the coverage of the solar spectrum is rather limited. One possible way of increasing the visible light response is to use supramolecules composed of several such chromophoric units [3].

Fig. 1 illustrates schematically the concept involved in the design of such 'antenna-sensitizer' systems employed in dye-sensitized photoelectrochemical cells. A polynuclear complex is constructed using different chromophores (labelled A, B and C in Fig. 1), each with maximal spectral response in a given region of the solar spectrum but together they cover the major part of the solar spectrum. With appropriate design of the bridging and spectator ligands, it is possible to have some internal energy ordering of the CT excited states of the three units. The lowest energy chromophore takes part in the key excited state charge injection process (central unit B in the case shown). The light energy absorbed by the peripheral units is transferred to the central chromophore B via intramolecular energy/electron processes. Thus optimal performance of light harvesting arrays requires good control of the intramolecular energy and electron transfer amongst the constituent units. This depends to a large extent on the nature of the bridge used to connect the various chromophoric units.

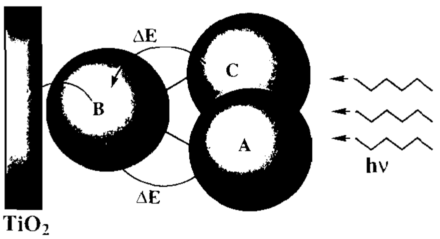

Fig. 1. Schematic representation of light-energy harvesting in dye-sensitized photoelectrochemical cells using polynuclear complexes.

The 'notion' of intramolecular processes assumes the supramolecule (e.g. $L_nM_1$–BL–$M_2L'_n$) to be made of some (well-defined) precursors and the validity of the following key assumptions: (i) the degree of electronic delocalization is sufficiently small for assignment of

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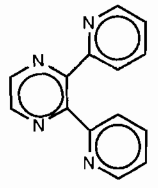
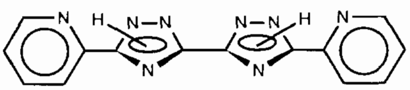
integral oxidation states to the metal centres ($M_1$ and $M_2$); (ii) selective excitation of the individual subunits is possible with appropriate choice of excitation wavelengths. Over the years, a number of experimental approaches has been developed to address the question of electronic coupling in such polychromophoric or supramolecular assemblies. One approach that dates to the early sixties involves the analysis of the absorption spectra of partially oxidized forms of ligand-bridged polynuclear complexes. Partially oxidized forms of polynuclear complexes (with metal centres in different oxidation states) often exhibit new optical charge transfer (intervalence transition (IT)) bands [4]. The energy, intensity and the bandwidth of metal-to-metal or intervalence charge transfer (MMCT or IT) transitions provide quantitative information on the nature and the extent of electronic communication through the bridge. A classical example is the Creutz–Taube ion, $[(NH_3)_5Ru-(pz)-Ru(NH_3)_5]^{5+}$, where pz = pyrazine [4f]. The $Ru^{II}$–$Ru^{III}$ complex shows an intense near-IR intervalence band with a maximum at 1570 nm ($\epsilon = 5000\ M^{-1}\ cm^{-1}$; $\Delta\nu_{1/2} = 1400\ cm^{-1}$).

After a brief survey of various bridging ligands that are currently available for the synthesis of light harvesting systems (Section 2) and of the principles of analysis of electronic coupling (Section 3), a comparative analysis is presented on what is known about the role of bridging ligands in modulating the electronic communication between the chromophores. The results obtained on complexes based on different bridges are highlighted, including those obtained in our laboratories on three bridging ligands: 2,3-bis(2-pyridyl)-pyrazine (dpp, **1**), and 5,5′-bis(2-pyridyl)-3,3′-bi(1,2,4-triazole) (BPBT, **2**) and cyanide (CN).



2,3-bis(2-pyridyl)-pyrazine (dpp) **1**



5,5′-bis(2-pyridyl)-3,3′-bi(1,2,4-triazole) (BPBT) **2**

Polynuclear complexes of the type $[(LL)_2M_1-(BL_1)-M_2(LL')_2]^{n+}$ and $[(X)(LL)_2M_1-(BL_2)-M_2(LL')_2-(BL_2)-M_3(LL'')_2(X)]^{n+}$, where LL, LL′, LL″ refer to bipyridine-type ligands (or non-chromophoric ones such as $Cl^-$, $H_2O$, $CN^-$, CO, ...); $BL_1$ represent bis-bidentate bridging ligands such as dpp or BPBT; $BL_2$ represent bis-monodentate such as cyanide; $M_1$, $M_2$ and $M_3$ stand for the metal centres (Ru(II), Os(II) and Re(I), have been examined. The chromophores employed are polypyridyl complexes of transition metal ions—those for which information on their properties as sensitizers, electron donor or acceptors is available. A comprehensive survey covering literature upto the late eighties is given in Ref. [5]. The discussion/analysis presented here is narrower in scope (restricted to symmetric, homo polynuclear complexes!), complementary to the earlier one and includes references to recent publications.

### 1.1. Nomenclature and notations

Table 1 contains a list of various bridging ligands used in the synthesis of polynuclear complexes and their possible modes of chelation. To facilitate the discussion, the following terminology will be used to distinguish various types of ligands (BL) and binuclear complexes $[(LL)_2M_1-BL-M_2(LL')_2]$. For ligands mono-, bi- or tetradentate refer to the presence of one, two or four chelation sites that can coordinate to a given metal ion. 2,2′-Bipyridine is labelled as a bidentate, in order to distinguish it from 4,4′-bipyridine which is a bis-monodentate. For complexes, the terms 'homo' and 'hetero' will be used to identify binuclear complexes with identical ($M_1 = M_2$) or different ($M_1 \neq M_2$) metal centres, respectively. The term 'symmetric' will refer to the case where the spectator ligands on the metal centres $M_1$, $M_2$ are identical and 'asymmetric' when they are different. Thus the complexes $[(bpy)_2Ru-dpp-Ru(bpy)_2]^{4+}$ and $[(Cl)(bpy)_2Ru-pz-Ru(bpy)_2Cl]^{2+}$ will be referred to as 'symmetric homo' dimers; $[(bpy)_2Ru-dpp-Os(bpy)_2]^{4+}$ as a symmetric hetero dimer; $[(CN)(bpy)_2Ru-CN-Ru(bpy)_2(H_2O)]^{2+}$ as a asymmetric homo dimer and $[(CN)(bpy)_2Ru\text{-}CN\text{-}Os(bpy)_2(H_2O)]^{2+}$ as an asymmetric hetero dimer. The oxidation state of various metal centres is indicated most often by arabic numerals, in the order of the metal centres separated by a comma. Thus [2,3] refers to oxidation state of 2+ and 3+ for the metal centres that are located at the left and right side of the bridging ligand/binuclear complex. [2,3,2] refers to a trinuclear complex wherein the centre metal ion is in the trivalent state while the two peripheral ones are divalent.

## 2. Features of the bridging ligands and the complexes

In this section a brief survey is given of the various bridging ligands made in recent years for the synthesis of polynuclear complexes. The ligands are grouped according to the type and the number of chelation sites available.

### 2.1. Bis-monodentate ligands

Most of the early work of Taube, Meyer and others [4,6] on ligand-bridged binuclear complexes involved bis-monodentate ligands such as pyrazine (**3**), pyrimidine (**4**), 4,4′-bipyridine (**5**), *trans*-1,2-bis(4-pyridyl)ethylene

Table 1
Polyimine-type of bridging ligands used in the synthesis of polynuclear complexes, their abbreviations and mode of chelation

| Ligand abbreviation[a] | Full description of the ligand | Type |
|---|---|---|
| bpa (**7**) | 1,2-bis(4-pyridyl)ethane | bis-monodentate |
| bpe (**6**) | *trans*-1,2′,bis(4-pyridyl)ethylene | bis-monodentate |
| 4,4′-bpy (**5**) | 4,4′-bipyridine | bis-monodentate |
| dppm | bis(diphenylphosphino)methane ($Ph_2PCH_2PPh_2$) | bis-monodentate |
| pym (**4**) | pyrimidine | bis-monodentate |
| pyzc | 2-pyrazinecarboxylate | bis-monodentate |
| pz (**3**) | pyrazine | bis-monodentate |
| apy (**17**) | aza-bis(2-pyridine) | bis-bidentate |
| BiBzIm (**16**) | 2,2′-bibenzimidazolate | bis-bidentate |
| bpbimH$_2$ (**28**) | 2,2′-bis(2-pyridyl)bibenzimidazole | bis-bidentate |
| bpt (**18**) | 3,5-bis(2-pyridyl)-1,2,4-triazole | bis-bidentate |
| bptz (**19**) | 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine | bis-bidentate |
| bpym (**15**) | 2,2′-bipyrimidine | bis-bidentate |
| 2,3′-dpp (or dpp) (**1**) | 2,3-bis(2-pyridyl)-pyrazine | bis-bidentate |
| 2,5-dpp (or bppz) | 2,5-bis(2-pyridyl)-pyrazine | bis-bidentate |
| dpbime (**29**) | 1,2-bis(2-(2-pyridyl)-benzimidazolyl)ethane | bis-bidentate |
| dpimbH$_2$ (**20**) | 2,6-bis(2-pyridyl)benzodiimidazole | bis-bidentate |
| dpq (or bpq) (**21**) | 2,3-bis(2-pyridyl)-quinoxaline | bis-bidentate |
| ppz | 4′,4′-phenanthrolino-5′,6′:5,6-pyrazine | bis-bidentate |
| hat (**22**) | 1,4,5,8,9,12-hexaazatriphenylene | tris-bidentate |
| tpbq (**23**) | 2,2′,3,3′-tetra(2-pyridyl)-6,6′-biquinoxaline | tetra-bidentate |
| bpbt (**2**) | 5,5′-bis(2-pyridyl)-3,3′-bi(1,2,4-triazole) | tetra-bidentate |
| tpp (**30**) | 2,3,5,6-tetrakis(2-pyridyl)pyrazine | bis-tridentate |
| tpbp (**27**) | 3,3′,5,5′-tetrapyridylbiphenyl | bis-tridentate |
| bpqp (**24**) | 6′,6″-bis(2-pyridyl)-quaterpyridine | bis-tridentate |
| btpbz (**25**) | 1,4-bis(2,2′:6′,2″-terpyridinyl)benzene | bis-tridentate |
| ttpbz (**26**) | 1,3,5-tris(2,2′:6′,2″-terpyridinyl)benzene | tris-tridentate |

[a] The number in parenthesis refers to the structure of the ligand referred to in the text at various places.

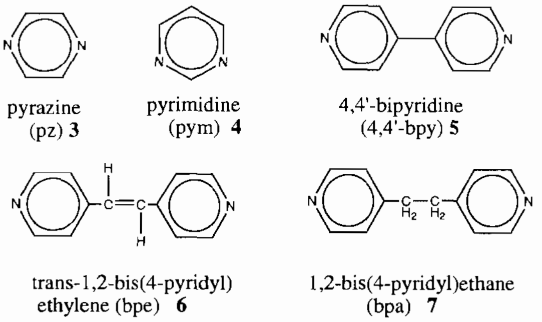
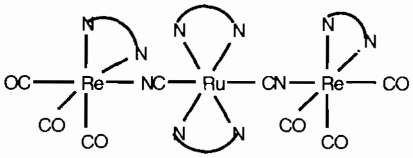
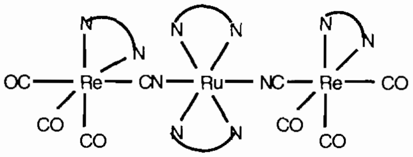

pyrazine (pz) **3**
pyrimidine (pym) **4**
4,4′-bipyridine (4,4′-bpy) **5**
trans-1,2-bis(4-pyridyl) ethylene (bpe) **6**
1,2-bis(4-pyridyl)ethane (bpa) **7**

Fig. 2.

(bpe, **6**) and 1,2-bis(4-pyridyl)ethane (bpa, **7**). Fig. 2 shows the structures of some of these simple bis-monodentate ligands. A ligand that has received significant attention in the studies of polynuclear complexes (in our laboratory and elsewhere) is the cyanide [7,8]. It is an asymmetric ligand. Using appropriate synthetic procedures, it is possible to make the structural isomers—cases where the same metal is C-bonded (nitrile mode) or N-bonded (isonitrile). Shown below schematically are two isomeric trinuclear complexes of this kind we examined recently [8b]. Complex **8** has the central Ru C-bonded while in **9** it is N-bonded.


**8**


**9**

Due to very high energies of the electronic transitions associated with the 'non-chromophoric' ligand(s), the lowest energy CT transitions in the polynuclear complexes are those associated with other polypyridine ligand(s). Even in homo binuclear complexes, significant differences exist between the C-bonded and N-bonded units. This is due to differences in the electron-donating capacity of the cyanide ligand as a nitrile or as isonitrile (the latter is a better donor). Partially oxidized forms of the cyano-bridged complexes have good stability and show strong inter-valence transitions in the red–near-

IR region. Agarwala and co-workers have shown [9] that chalcogenocyanate ions such as $SeCN^-$ and $SCN^-$ can also act as useful bridging ligands. Unlike in cyanide, the electron donor capacities of S/Se and N are not very different. This leads to much smaller $\Delta E$ values between the first and second oxidation potentials in the homo symmetric dimers. Alicyclic disulfides have also been used in a similar manner [10].

### *2.2. Bis- and higher oligomeric bidentate ligands*

The simplest form of multi-bidentate ligand is one where two or more molecules of 2,2′-bipyridine are connected together through some spacer or connector units. Tinnemans [11], Schmehl [12], Rillema [13] and co-workers have prepared a number of bis(bipyridines) linked by poly-methylenes (**10**) or poly-oxyethers (**11**,**12**). Ziessel and Lehn [14] have described synthetic procedures for the preparation of ligands bearing two to six pendant, unsubstituted/substituted 2,2′-bipyridine groups attached to the acyclic tripode **13** or a tetrapode such as macrocyclic polyamines (trianonadecane, cyclam, hexacyclam, ...). Vögtle and co-workers [15] have used benzene or triphenylbenzene as the connector to make tripodes (**14**) carrying three bipyridine molecules. Fig. 3 shows the structures of some of these linked 2,2′-bipyridine ligands.

Most of the studies of Ru complexes in the eighties were concerned with tunability of photophysical and redox properties using polypyridines or polyimines in general. These studies are being extended to larger templates composed of these simple polyimines. Typical examples of this kind are 2,2′-bipyrimidine (bpym, **15**) [16], 2,2′-bibenzimidazolate (BiBzIm, **16**) [17,18], azo-bis(2-pyridine) (apy, **17**) [19], 3,5-bis(2-pyridyl)-1,2,4-triazole (bpt, **18**) [20], 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz, **19**) [19], 2,6-bis(2-pyridyl)benzodiimidazole (dpimb$H_2$, **20**) [17] and 2,3-bis(2-pyridyl)quinoxaline (dpq, **21**) [21]. Fig. 4 shows the structures of the bidentate bridging ligands referred to above.

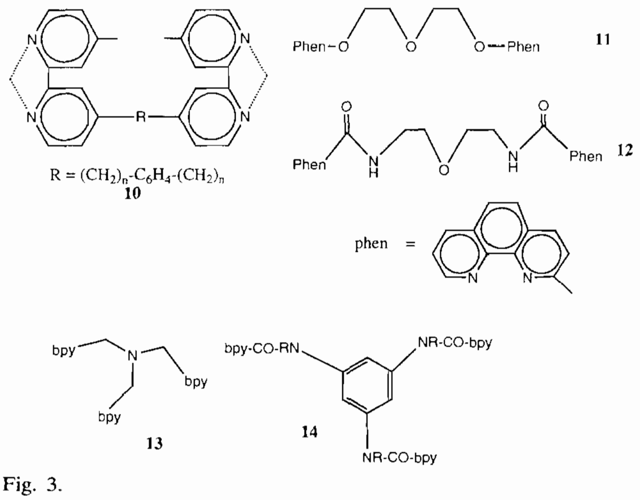
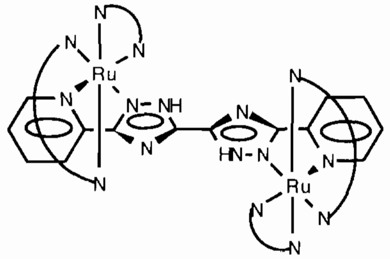
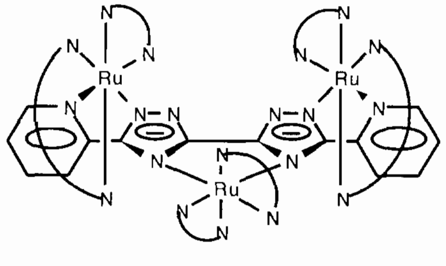


Fig. 3.



$[(bpy)_2Ru^{II}]_2(BPBTH_2)^{4+}$ [2,2]



$[(bpy)_2Ru^{II}]_3(BPBT)^{4+}$ [2,2,2]

Bis(pyridyl)-bi(triazole) (bpbt, **2**) we examined recently is an octadentate polyimine, potentially capable of chelating up to four metal centres. We have only been successful in making the bi- and trinuclear complexes [22]. Synthesis of the tetranuclear complex was unsuccessful presumably due to steric constraints (crowding). The structures above show the mode of coordination in the bi- and trinuclear complexes. It can be seen that the two terminal pyridyl-triazoles coordinate the metal ion sequentially before the third

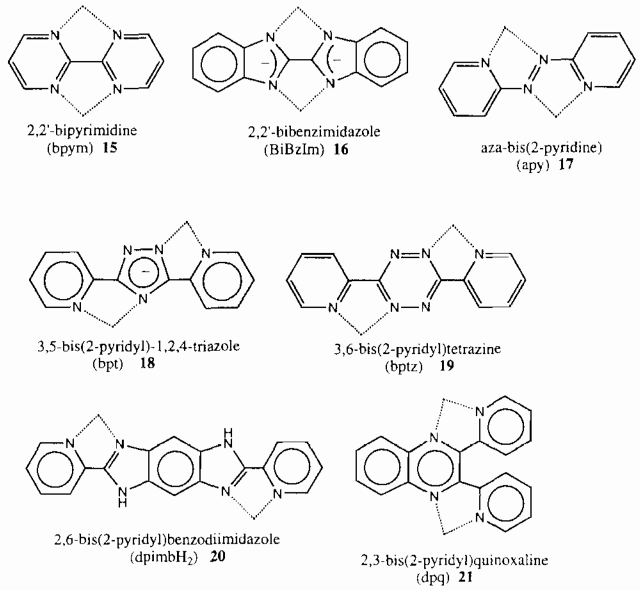
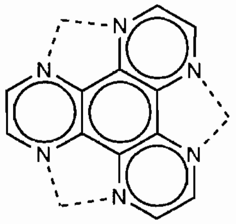
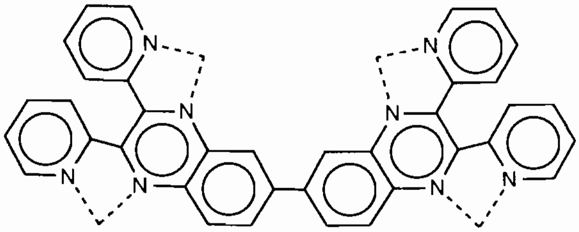


Fig. 4.

metal ion coordinates at the centre. The two metal centres in the binuclear complex are farther apart compared to those in the trinuclear one. Bpbt is an electron-rich ligand, more difficult to reduce when compared to bipyridine. Consequently the lowest CT excited state in bpbt complexes is M-bpy and not M-bpbt. As in the case of cyano-bridged ones, partially oxidized forms of the bi- and trinuclear complexes show strong IT bands in the red–near-IR region. The bpbt ligand can be considered as an extended version of the bis(2-pyridyl)-1,2,4-triazole (bpt) examined earlier by Reedijk and co-workers [20]. In bpbt, the first two coordination sites are identical while the third one is significantly different from the first two (ligand takes on a third metal as a dianion). The bpt ligand can also be considered as an unsymmetrical bridging ligand due to the non-equivalence of 1- (or 2) and 4-nitrogens of the triazole ring. This may account for the non-equivalence of the energy levels of the two $Ru(bpy)_2$ fragments.



1,4,5,8,9,12-hexaazatriphenylene (hat) **22**



2,2',3,3'-tetra(2-pyridyl)-6,6'-biquinoxaline (tpbq) **23**

The polycyclic 1,4,5,8,9,12-hexaazatriphenylene (hat, **22**) is an interesting tris-bidentate capable of chelating three metal centres. Kirsch-De Mesmaeker and co-workers have studied a number of hat-based complexes [23]. By linking back-to-back two molecules of bis(2-pyridyl)quinoxaline, Rillema et al. [24] made the tetra(pyridyl)biquinoxaline (tpbq, **23**) which is a tetra-bidentate. Since this structure is a duplication of the dpq ligand, it is possible to prepare tetranuclear complexes.

A tetraimine bridging ligand, used by us and several others, is 2,3-bis(2-pyridyl)pyrazine (dpp, **1**) [25–27]. The four nitrogens are located in such a way that this ligand behaves as a bis-bidentate. The simplest binuclear complex derived using this ligand is $[(bpy)_2Ru\text{-}dpp\text{-}Ru(bpy)_2]^{4+}$. By successive replacement of the bpy ligand by the bridging ligand dpp in $Ru(bpy)_3{}^{2+}$ or $[(bpy)_2Ru\text{-}dpp\text{-}Ru(bpy)_2]^{4+}$ it is possible to build higher polynuclear complexes. In a number of publications, Balzani and co-workers [27] have demonstrated the design of such potential light harvesting systems:

$$Ru(dpp)_3{}^{2+} + 3Ru(bpy)_2X_2 \longrightarrow Ru[(dpp)Ru(bpy)_2]_3{}^{8+} + X^- \quad (1)$$

$$Ru(dpp)_3{}^{2+} + 3Ru[(dpp)Ru(bpy)_2]_2Cl_2{}^{4+} \longrightarrow Ru\{(dpp)Ru[Ru(dpp)Ru(bpy)_2]_2\}_3{}^{20+} + X^- \quad (2)$$

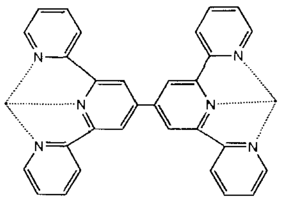
By concurrent variation of the metal centres and/or the spectator ligand bpy by other chromophoric or non-chromophoric ligands, it is possible to introduce some relative energy ordering amongst the various chromophoric units of the supramolecule. In the case of dpp-bridged complexes such as $[(bpy)_2Ru\text{–}dpp\text{–}Ru(bpy)_2]^{4+}$, by using techniques such as resonance Raman spectroscopy, it is possible to distinguish the CT bands associated with the bridging ligand from those involving the spectator ones [28]. The lowest energy CT transition most often is associated with the bridging ligand (Ru–dpp CT) and not with the bipyridine (Ru–bpy). This is due to very good electron accepting properties of the bridging polyimine ligand as compared to the spectator ligand (bpy). Partially oxidized forms do not have sufficient stability for extensive quantitative studies to be made.

### *2.3. Bis- and higher oligomeric tridentates*

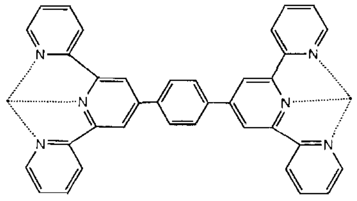
A number of templates has been made based on the tridentate terpyridine ligands, particularly by Constable et al. [29]. These include back-to-back 2,2′:6′,2″-terpyridine (bpqp, **24**) and two/three terpyridine units connected through a benzene ring (btpbz, **25**; ttpbz **26**). Fig. 5 shows the structures of these bridging ligands. Possible extensions of these to make one-dimensional linear polymers have also been described. The template 3,3′,5,5′-tetrapyridylbiphenyl (tpbp, **27**) is an ortho-metalling ligand and behaves like a bis-tridentate (i.e. as back-to-back bis(terpyridine)) [30,31].

## 3. Electronic coupling of chromophoric units

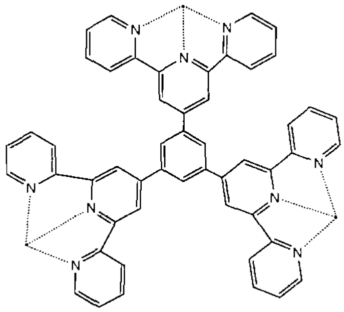
Charge localization in polynuclear complexes has been examined within the framework of electron transfer theory by Hush and others [4]. The case of intramolecular electron transfer in the partially oxidized form of the binuclear complex $[L_nM_1\text{–}BL\text{–}M_2L'_n]$ is taken as an example. The extent of electronic coupling/metal–metal interaction depends on the relative mag-



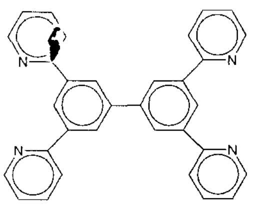
6,6'-bis(2-pyridyl)-2,2':4',4'':2'',2'''-quaterpyridine (bpqp) **24**



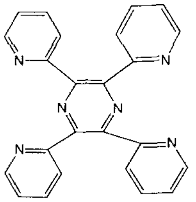
1,4-bis(terpyridinyl)-benzene (btpbz) **25**



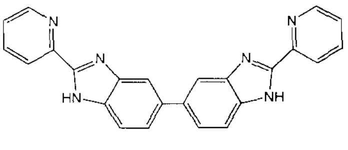
1,3,5-tris(terpyridinyl)-benzene (btpbz) **26**



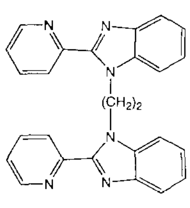
3,3',5,5'-tetra(2-pyridyl)biphenyl tpbq **27**



2,3,5,6-tetrakis(2-pyridyl)pyrazine tpp **30**



2,2'-bis(2-pyridyl)bibenzimidazole bpbimH$_2$ **28**



1,2-bis(2-pyridyl)-benzimidazolyl)ethane dpbime **29**

Fig. 5.

nitudes of the perturbation Hamiltonian $H_{AB}$ coupling the initial ($M_1$–BL–$M_2$) and the final ($M_1^+$–BL–$M_2^-$) states and the reorganization energy $\lambda_{AB}$ available for the charge redistribution process. The classification proposed by Robin and Day [4b] is generally used to describe various situations. Class I type refers to the case where there is no interaction between the metal centres ($H_{AB}=0$). In this 'valence-localized' case, the two metal centres can be assigned integral oxidation states such as 2+ and 3+. In the case of very strong interaction and consequent delocalization of charges over the entire supramolecule ($H_{AB} \geqslant \lambda$), the system is labelled as Class III. In this extreme ('valence-delocalized') scenario, a species with a non-integral oxidation state would result.

The majority of systems fall in the intermediate case, weak to moderate interactions ($H_{AB} \leqslant \lambda$) and these are referred to as Class II type systems. The system can be considered as perturbed cases of Class I, i.e. localized electronic states leading to integral oxidation states. Fig. 6 presents schematically the relative disposition of potential energy surfaces for the initial and final states for electron transfer in symmetrical binuclear complex of Class II. In ligand-bridged complexes, the extent of metal–metal interactions in general, depends on (i) the distance between the metal centres, (ii) the ability of the bridging ligand in delocalizing the electronic charge and (iii) the coordination environment of the metal ions. We will consider some of the experimentally available properties for examining the electronic coupling between the various units.

### *3.1. Redox properties*

In the absence of any electronic coupling, similar metal centres in a polynuclear complex are expected to undergo oxidation at nearly the same oxidation potential. Any metal–metal interaction leads to asymmetry and the existence of discrete oxidation waves for each metal centre. When there is electronic communication through the bridge, removal of charges at one part is felt by the entire supramolecule. A large $\Delta E$ thus indicates net stabilization of the partially oxidized form with respect to possible comproportionation. For a binuclear complex [2,2], the latter refers to the process:

$$[2,3]+[2,3] \longrightarrow [3,3]+[2,2] \tag{3}$$

An estimate of the comproportionation constant ($K_{com}$) can be obtained from the successive one-electron oxidation potentials ($\Delta E$).

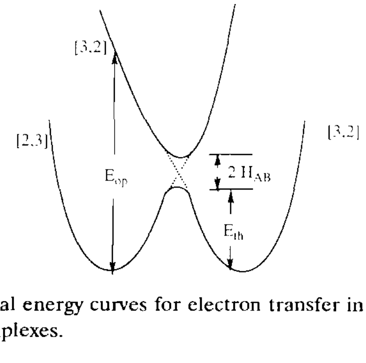


Fig. 6. Potential energy curves for electron transfer in ligand-bridged binuclear complexes.

$$K_{com}=\exp(\Delta E/25.69) \qquad (4)$$

A large $K_{com}$ can also be taken to indicate 'good electronic communication' between the metal centres.

A comparison of the electrochemical properties of the polynuclear complex with those of appropriate precursor/model compounds can also be used as a way of assessing electronic coupling. With bridging ligands that are good $\pi$-acceptors (as in the case of polyimines such as bis(pyridyl)pyrazine) there is substantial lowering of the ligand $\pi^*$-orbitals upon chelation of one metal centre and hence the chelation of the second metal does not occur under these conditions present for the first one. Electrochemical measurements provide qualitative information on this.

### 3.2. Photophysical properties

Chromophoric units considered in this paper are based on polypyridine complexes with metal centres such as Ru or Os. They show intense MLCT absorption bands in the visible and moderate emission in fluid solutions at room temperature. Useful correlations have been established earlier between the photophysical properties (absorption/emission) with electrochemical properties (oxidation/reduction potentials) of mononuclear complexes [2]. In polynuclear complexes these can be used to interpret the observed properties, especially spectral shifts upon multinucleation.

Depending on the electronic nature of the bridge and the non-bridging ('spectator') ligands, the lowest excited state in polynuclear complexes can be metal-to-bridging ligand charge transfer (M → BL CT) or metal-to-spectator CT (M → L CT). The former occurs with bridges that are good $\pi$-acceptors and the latter type is seen with bridges that are non-chromophoric (such as cyanide) or electron-rich (bpt, BiBzIm, ...). The bis-monodentate ligand 4,4′-bipyridine is an interesting case. With suitable choice of spectator ligands, it is possible to choose the lowest excited state to involve the bridge or the non-bridging ones. These differences have important implications on the photostability of the polynuclear complexes (decomposition via ligand substitution or subsequent to electron transfer).

The charge transfer absorption bands of polynuclear complexes in the visible light region often consist of overlapping bands corresponding to various CT transitions. Assignment of the bands requires monitoring of the emission at several excitation wavelengths. The assumption most often made is that the polynuclear complexes fall under 'localized' description that allows selective excitation of one chromophore. The choice of excitation wavelengths can be made by reference to the mononuclear complex or appropriate model compounds. Alternatively other spectroscopic techniques (such as resonance Raman spectroscopy) can be used to assess the relative contributions of various CT transitions within the broad band. Assignment of the emission is also made by comparative analysis. The observed absorption and emission in the polynuclear complex is the complex outcome of changes in the oxidation, reduction potentials, operation of energy gap law and possible quenching. Interpretation is by no means trivial. Interpretations of these properties as indicative of the extent of electronic communications must be done with caution, as will be shown. But this exercise is essential, for they form the basis of further studies of intramolecular electron and energy transfer in asymmetric or hetero polynuclear complexes. Photophysical studies are important for understanding the functioning of the light harvesting mechanism.

### 3.3. Intervalence transitions (IT)

By adding controlled amounts of oxidants such as bromine or Ce(IV) it is possible to generate partially or fully oxidized forms of the bi- and trinuclear complexes in acetonitrile (obviously for Class II and Class III candidates). As mentioned earlier, in a number of cases, partially oxidized forms show broad, structureless bands in the near-IR region (7000–10 000 cm$^{-1}$). These bands are due to optically induced electron transfer from one end of the molecule to the other (interconversion of the redox isomers):

$$[(X)(LL)_2M_1^{II}\text{–}BL\text{–}M_2^{III}(LL)_2] \longrightarrow [(X)(LL)_2M_1^{III}\text{–}BL\text{–}M_2^{II}(LL)_2]$$

These metal-to-metal charge transfers (MMCT) are most commonly referred to as intervalence transitions (IT). Assuming weak electronic coupling and the classical limit, Hush has derived the following expressions relating the internal energy difference between the two redox isomers ($\Delta E$), optical band energy ($E_{op}$) as given by the band maximum ($\nu_{max}$) and bandwidth at half-height ($\Delta\nu_{1/2}$) of the IT band.

$$\Delta\nu_{1/2}=2310(E_{op}-\Delta E) \qquad (5)$$

$$=(2310\nu_{max})^{1/2} \qquad (6)$$

The intensity of the optical electron transfer band is related to the magnitude of the electronic coupling matrix element $H_{AB}^{el}$.

$$\epsilon_{max}=[2380r^2(H_{AB}^{el})^2]/(E_{op}\Delta\nu_{1/2}) \qquad (7)$$

In the above expression $\epsilon_{max}$ refers to molar absorption coefficient, $r$ (Å) is the intercomponent distance and $E_{op}$, $\Delta\nu$ are in units of cm$^{-1}$. Thus a strong IT band is indicative of significant communication between the metal centres. The degree of electron delocalization $\alpha^2$ can be computed using the expression

$$\alpha^2 = 4.2\times10^{-4}\epsilon_{\max}\Delta\nu_{1/2}/\nu_{\max}r^2 \qquad (8)$$

By definition, Class I compounds do not have any stability in the mixed valence form and hence show no IT bands. Class III compounds show intense IT bands that are fairly narrow ($\epsilon \geqslant 5000$ M$^{-1}$ cm$^{-1}$; $\Delta\nu_{1/2} \leqslant 2000$ cm$^{-1}$). Class II compounds show comparatively weaker bands with larger bandwidths ($\epsilon \leqslant 5000$ M$^{-1}$ cm$^{-1}$; $\Delta\nu_{1/2} \geqslant 2000$ cm$^{-1}$). The energy of the IT is solvent dependent and quantitative analysis of this solvent dependence can provide estimates of the matrix coupling element $H_{AB}$.

### *3.4. Transient formation of mixed valence species*

It is well known that excitation of polypyridyl complexes of Ru(II) to the CT excited state, in effect creates an oxidized metal centre (Ru$^{III}$) and a reduced ligand (LL$^{\cdot-}$).

$$[\mathrm{Ru^{II}(LL)_3}]^{2+} \xrightarrow{h\nu} [\mathrm{Ru^{III}(LL)_2(LL^{\cdot-})}]^{2+}\,{}^{*} \qquad (9)$$

In polynuclear complexes this transient hole, like the chemically oxidized metal centre, can give rise to intervalence transitions with the adjacent non-oxidized metal centres (Eqs. (10) and (11)).

$$[\mathrm{(X)(bpy)_2M_1{-}BL{-}M_2(bpy)_2(X)}] \xrightarrow{h\nu}$$
$$[\mathrm{(X)(bpy)_2M_1{-}BL{-}M_2{}^{+}(bpy)(bpy^{\cdot-})(X)}]^{*} \qquad (10)$$

$$[\mathrm{(X)(bpy)_2M_1{-}BL{-}M_2{}^{+}(bpy)(bpy^{\cdot-})(X)}]^{*} \xrightarrow{\mathrm{IT}}$$
$$[\mathrm{(bpy)_2M_1{}^{+}{-}BL{-}M_2(bpy)(bpy^{\cdot-})(X)}]^{*} \qquad (11)$$

Detection of such intervalence transition bands in the excited state absorption spectra of polynuclear complexes containing MLCT excited states is of great mechanistic interest. There have been only a few flash photolysis studies of this kind.

## 4. Non-interacting (or very weakly interacting systems (Class I)

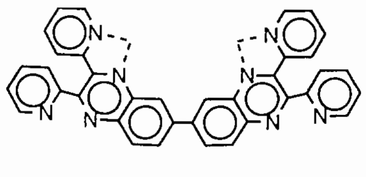
Let us consider the simplest case of symmetric homobinuclear complexes (same metal centre and spectator ligands on either side of the bridging ligand). In the absence of any metal–metal interaction, the polynuclear complex behaves as a cluster of several mononuclear units. The absence of electronic coupling is indicated by striking similarity in the properties (oxidation and reduction potentials, lowest energy CT absorption and emission maxima) of the mononuclear one and the bi/higher oligomeric units. With no significant spectral shift, the molar absorbances at the MLCT maxima increase linearly with the number of chromophoric units (metal centres) present. Similarly, multi-electronic oxidation and/or reduction is observed in electrochemical studies. A two-electron oxidation is expected for the binuclear, a three-electron wave for the trinuclear complex and so on. Herein we also consider cases where there is very weak coupling. For the sake of classification, we consider here cases in which the difference between the first and second oxidation in the binuclear complex ($\Delta E$) is $\leqslant 100$ mV. When $\Delta E$ is less than 50 mV, it is not possible to observe discrete oxidation waves, instead one observes large anodic–cathodic peak separation. By simulation it can be shown that the peak separation can be as large as 100 mV for $\Delta E \approx 35$ mV.

When the two chromophoric units are linked by long covalent bridges as in the case of long methylene chains, then the interactions between the chromophores (through bond or through space) become negligible. Bridges **10–14**, **24–26** referred to earlier are representative ones and Table 2 provides representative data on these complexes. The observed properties are as per the expectations elaborated above. It is remarkable that the four Ru centres in the tetranuclear complex [(Me$_2$-bpy)$_2$Ru(**10**)]$_3$Ru$^{8+}$ and the three Ru centres in the tripod complex [(bpy)$_2$Ru]$_3$(**13**)$^{6+}$ undergo oxidation at a nearly identical potential. For the mono-, bi- and trinuclear complexes of the tripod **14**, Balzani and coworkers have observed [15] nearly identical photophysical and redox properties. Constable and Cargill Thompson [29a] have examined a number of bi- and trinuclear complexes based on linked 2,2′:6,2′-terpyridines of the bipode and tripode type. Using a series of 4′-X-terpy (X = H, Cl, Ph, EtO, MeS, OH, NMe$_2$) as spectator ligands, it was possible to tune the spectral and redox properties of the polynuclear complexes. When the oxidation potentials of the bi- and trinuclear complexes are plotted against the Hammett $\sigma^+$ parameter for the substituent X, straight lines can be fitted to the data. Thus the bipode and tripode ligands effectively behave as a simple 4′-phenyl substituted terpy and there is no effective electronic interaction between the substituents or the metals coordinated to them.

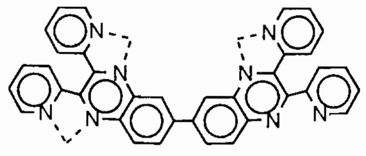
The multidentate bridging ligand system tpbq (**23**) studied by Rillema et al. [24] illustrates the possible case where one can sequentially build polynuclear complexes. The second metal centre in the binuclear complex chelates at the far-end of the molecule. The mono- and binuclear complexes show nearly identical oxidation potentials (= 1.41 V), the latter corresponding to a single two-electron oxidation. The large distance of separation between the two Ru(bpy)$_2$ units and free rotation around the C–C bond of the biquinoxaline reduce any electronic communication through the bridge to negligible amounts. In the tri- and tetranuclear complexes, the third and fourth Ru(bpy)$_2$ units are present on either side of the pyrazine unit (as in the case of dpp-bridged complexes). The complexes show two oxidation waves: one $2e^-$ and one $1e^-$ for the

Table 2
Absorption spectral and redox properties of ligand-bridged complexes of very weakly coupled systems

| Complex | MLCT abs. max. (nm) $\epsilon$ ($M^{-1}$ $cm^{-1}$) | $E_{ox}$ (V vs. NHE) (No. electrons) | Ref. |
|---|---|---|---|
| $[(Me_2bpy)_2Ru(\mathbf{10})]^{2+}$ | 461(14130) | +1.11 (1e) | [12] |
| $[\{(Me_2bpy)_2Ru\}_2(\mathbf{10})]^{4+}$ | 461(27540) | +1.11 (2e) | [12] |
| $[\{(Me_2bpy)_2Ru(\mathbf{10})\}_3Ru]^{8+}$ | 462(60250) | +1.11 (4e) | [12] |
| $[\{(bpy)_2Ru\}_2(\mathbf{11})]^{4+}$ | 453(29500) | +1.47 (2e) | [11] |
| $[\{(bpy)_2Ru\}_2(\mathbf{12})]^{4+}$ | 446(31600) | +1.46 (2e) | [11] |
| $[\{(bpy)_2Ru\}_3(\mathbf{13})]^{6+}$ | 446(33000) | +1.46 (3e) | [14] |
| $[\{(bpy)_2Ru\}(tpbq)]^{2+}$ | 525(8490) | +1.41 (1e) | [24] |
| $[\{(bpy)_2Ru\}_2(tpbq)]^{4+}$ | 528(16300) | +1.42 (2e) | [24] |
| $[\{(bpy)_2Ru\}_3(tpbq)]^{6+}$ | 542(17400), 616(20400) | +1.41 (2e), 1.63 | [24] |
| $[\{(bpy)_2Ru\}_4(tpbq)]^{8+}$ | 453(29500), 622(34000) | +1.41 (2e), 1.63 (2e) | [24] |
| $[(\phi\text{-terpy})_2Ru]^{2+}$ | 488(26600) | +1.46 (1e) | [29] |
| $[\{(terpy)Ru\}_2(btpbz)]^{4+}$ | 492(44300) | +1.46 (2e) | [29] |
| $[\{(terpy)Ru\}_3(ttpbz)]^{6+}$ | 487(65900) | +1.43 (3e) | [29] |



[2------2]



[2,2-----2]

trinuclear complex and two $2e^-$ for the tetranuclear case. The tri- and tetranuclear complexes can be represented as [2,2---2] and [2,2---2,2] where the dashed line acknowledges the fact that the metal centres are held together by a bridging ligand but the interaction between the metal centres is at best very weak.

Amongst the bis-monodentates, complexes derived using 4,4′-bpy, bpe and bpa show very weak metal–metal interactions. In their studies of $[(Cl)(bpy)_2Ru\text{–}BL\text{–}Ru(bpy)_2(Cl)]^{2+}$, BL = 4,4′-bpy (**5**), bpe (**6**) and bpa (**7**), Powers and Meyer [6b] observed only one wave in the potential region upto 1.4 V. The peak separations are considerably larger than the theoretically predicted 59 mV. The large peak separation waves result from close proximity of two closely spaced one-electron waves. The $\Delta E_{1/2}$ values are estimated to be in the range of ≈50 mV.

Free rotation around the C–C bond is feasible in the bridging ligands based on back-to-back linking of 2-pyridylbenzimidazole ($bpbimH_2$, **28**) or one where two benzimidazoles are linked by a ethane bridge (dpbime, **29**) which allows minimal inter-chromophore interaction. The metal–metal interactions thus are very weak in the binuclear complcxes $[M(bpy)_2]_2BL$, where BL = $bpbimH_2$ or dpbime; M = Ru(II), Os(II) [17]. A $\Delta E_{1/2}$ value of ≈50 mV has been estimated for the dpbime case. When the bridge is in the deprotonated form (bpbim), $\Delta E$ is ≈80 mV for the bis(Ru) case and decreases to 40–50 mV upon protonation ($bpbimH_2$). Clearly deprotonation of the bridging ligand relatively stabilizes the mixed valence complexes. There have also been a few other cases involving this type of proton effect on modulating the electronic coupling Krentzien and Taube [32] found that the electronic coupling in pentaammine ruthenium complexes with malonitrile increased upon deprotonation of the bridge. Reedijk and co-workers [33] have observed similar pH effects on the binuclear complexes of bis(pyridyl)-triazole.

### 4.1. Excited state interactions

The process of energy migration in a collection of identical chromophores is an important one that can affect the overall efficiency of plant photosynthesis. There has been a lot of interest in the excited state annihilation processes that can occur in the light harvesting part of the thylakoid membranes (assembly of chlorophyll molecules). There have been few studies of excitonic effects in synthetic porphyrin dimers and oligomers. In Class I type polynuclear complexes, one has a similar collection of identical chromophores. Excited state interactions in such assemblies have not yet been fully investigated. Due to isoenergetic situation of the lowest energy excited state, selective excitation of one chromophore in the assembly is not possible. However, the excited state is expected to have strong intensity dependent effects, particularly quenching by the unexcited state. Electronically excited states can be quenched by unexcited ground state units or even by another excited state (triplet–triplet annihilation).

Occurrence of such triplet–ground state and triplet–triplet annihilation reactions are known in concentrated solutions of porphyrins, porphyrin arrays and are well documented. The feasibility and extent of such reactions can be judged by appropriate thermodynamic analysis.

There have been only a few quantitative studies of intensity dependence of luminescence yield, lifetime and excited state absorption in ligand-bridged polynuclear complexes. As mentioned earlier, most often emission lifetimes are made at very low excitation/photon flux. Multiple excitations are thus avoided and single exponential decays are observed. Similar excited state lifetimes measured for the monomer and dimer in such cases suggest that quenching by ground state chromophores is inefficient. In their studies of the tetranuclear complex, $[(bpy)_2Ru(\mathbf{10})]_3Ru^{8+}$, Schmehl et al. [12] noted strange results: the emission lifetime of the tetranuclear complex was similar to that of the monomer, yet the emission yield for the former decreased to ≈60%. Ohno et al. [17e] recently examined the efficiency of the formation of the MLCT excited state of the mono- and binuclear complexes $[(bpy)_2Ru]_n(dpbime)^{2n+}$ ($n=1,2$) by monitoring the transient absorption as a function of the excitation laser intensity. The excitation efficiency of the metal sites in the binuclear case was found to be lower than 50% when the laser power was large enough to excite more than 80% of the mononuclear complex. The low efficiency has been attributed to annihilation of the excited states.

## 5. Weakly interacting systems (Class II) involving polyimine bridges

Meyer and co-workers made a systematic study of metal–metal interactions in the complexes $[(Cl)(bpy)_2Ru–BL–Ru(bpy)_2(Cl)]^{2+}$, where BL is a series of bis-monodentate ligands. As mentioned earlier, 4,4′-bpy, bpe and bpa can be considered as very weakly interacting ($\Delta E \leqslant 100$ mV). Weak interactions can be seen for pz, pym ($\Delta E \approx 120$ mV) and for dppm (≈140 mV) [6]. Table 3 presents data on the first and second oxidation potentials for a number of binuclear complexes based on polyimine type ligands. These are cases where there is significant stabilization of the partially oxidized complexes.

Examination of the data collected in Table 3 shows important trends in the extent of bridging ligand communication in various cases. A comparison of the $\Delta E_{1/2}$ values for different bridging ligands in $[Ru(bpy)_2]_2BL$ allows a relative ordering of *destabilization* of the resulting mixed valence complex [2,3]: 4,4′-bpy > pym > pz > bpym > 2,3-dpp > 2,5-dpp > pyzc > ppz > bppz > abpy. For a given bridging ligand (dpp for example), replacement of Ru(II) by Os(II) leads to a significant increase in $\Delta E_{1/2}$ indicating effective stabilization/delocalization of charges in Os. A similar trend can be seen when the bpy ligand is replaced by phen, a ligand with a larger $\pi$-system. An inverse trend is observed in cases where the bridging ligand is electron-rich and the lowest excited state is associated with M–bpy and not M–BL. Typical examples are bis(2-pyridyl)-1,2,4-triazole (bpt) or biimidazole ($BiimH_2$). The $\Delta E_{1/2}$ values are smaller for Os complexes as compared to those with Ru centers. More dramatic effects are seen when ammonia ligands replace bpy. Replacement of competitive $\pi$-backbonding bpy ligands by $NH_3$ in $[(NH_3)_4Ru–dpp–Ru(NH_3)_4]^{4+}$ leads to $\Delta E_{1/2} \approx 0.39$ V, comparable to that observed in the analogous Creutz–Taube ion, $[(NH_3)_5Ru–pz–Ru(NH_3)_5]^{4+}$. Similarly larger differences are observed when chloride ions are present.

Goldsby and Meyer [6e] cite four factors that can contribute to the non-zero values of the $\Delta E_{1/2}$ in symmetric homo dimers: (i) electrostatics or ionization energies – since the second oxidation occurs adjacent to a greater positive charge than the first oxidation, it will occur at a higher potential; (ii) solvation energies – the solvation energies will be different for the $Ru^{II}–Ru^{II}$, $Ru^{II}–Ru^{III}$, $Ru^{III}–Ru^{III}$ dimers; (iii) delocalization or resonance – the unpaired electron is partially delocalized onto the Ru(III) site, shifting the second oxidation to potentials higher than one would expect with a totally localized electron; (iv) statistical contributions – the $Ru^{II}–Ru^{II}$ dimer can be oxidized to give either $Ru^{II}–Ru^{III}$ or $Ru^{III}–Ru^{II}$ and the $Ru^{III}–Ru^{III}$ dimer reduced to give either $Ru^{II}–Ru^{III}$ or $Ru^{III}–Ru^{II}$.

The ionization energy term leads to an increase in $\Delta E_{1/2}$ as the distance between the metal sites is decreased while the solvation energy term varies in the opposite sense. The magnitude of the resonance energy term depends explicitly on the electronic properties of the metal ions and the bridging and the peripheral ligands. For asymmetric and/or hetero dimers, the effects of ionization energy, solvation energies and delocalization will also determine the magnitude of $\Delta E_{1/2}$. In a number of cases the major contributor to the large $\Delta E_{1/2}$ values is the electrostatic term and the magnitude of delocalization or resonance term is rather small. The intensity of the intervalence transition band in the corresponding mixed valence compounds is a good measure of the latter.

The tetranuclear complex $Ru[(dpp)Ru(bpy)_2]_3^{8+}$ derived from $Ru(dpp)_3^{2+}$ [26] can be considered to be made up of two types of chromophores: three peripheral $Ru(bpy)_2(dpp)$ type units and a central $Ru(dpp)_3$ type unit. The lowest energy oxidation is a single peak at +1.62 V associated with the three peripheral Ru centers. No oxidation of the core $Ru(dpp)_3$ unit was observed within the solvent window (≈2.0 V versus SCE) which

Table 3
Successive oxidation potentials and their difference ($\Delta E_{1/2}$) values for various polyimine-bridged symmetric homo binuclear complexes (in acetonitrile)

| Complex | $E_{1/2}(1)$ (V) | $E_{1/2}(2)$ (V) | $\Delta E_{1/2}$ (mV) | Ref. |
|---|---|---|---|---|
| $[(bpy)_2Ru-apy-Ru(bpy)_2]^{4+}$ | 1.67 | 2.22 | 550 | [19] |
| $[(bpy)_2Ru-bptz-Ru(bpy)_2]^{4+}$ | 1.52 | 2.02 | 500 | [19] |
| $[(bpy)_2Ru-BiBzIm-Ru(bpy)_2]^{2+}$ | 0.77 | 1.06 | 290 | [17] |
| $[(bpy)_2Ru-bpt-Ru(bpy)_2]^{3+}$ | 1.04 | 1.34 | 300 | [20] |
| $[(bpy)_2Ru-hat-Ru(bpy)_2]^{4+}$ | 1.53 | 1.78 | 250 | [23] |
| $[(phen)_2Ru-dpp-Ru(phen)_2]^{4+}$ | 1.44 | 1.65 | 210 | [25–27] |
| $[(bpy)_2Ru-ppz-Ru(bpy)_2]^{4+}$ | 1.32 | 1.52 | 200 | [26] |
| $[(bpy)_2Ru-bpym-Ru(bpy)_2]^{4+}$ | 1.53 | 1.69 | 160 | [16] |
| $[(bpy)_2Ru-tpbq-Ru(bpy)_2]^{4+}$ | 1.43 | 1.60 | 170 | [24] |
| $[(bpy)_2Ru-dpp-Ru(bpy)_2]^{4+}$ | 1.38 | 1.56 | 180 | [25–27] |
| $[(phen)_2Ru-dpq-Ru(phen)_2]^{4+}$ | 1.48 | 1.64 | 160 | [21] |
| $[(bpy)_2Ru-bpbtH_2-Ru(bpy)_2]^{4+}$ | 0.85 | 1.01 | 160 | [22] |
| $[(bpy)_2Ru-dpq-Ru(bpy)_2]^{4+}$ | 1.47 | 1.62 | 150 | [21] |
| $[(bpy)_2Ru-2,5\text{-}dpp-Ru(bpy)_2]^{4+}$ | 1.39 | 1.58 | 190 | [19] |
| $[(bpy)_2Os-dpp-Os(bpy)_2]^{4+}$ | 0.83 | 1.12 | 250 | [25–27] |
| $[(bpy)_2Os-bpt-Os(bpy)_2]^{3+}$ | 0.64 | 0.85 | 210 | [20] |
| $[(bpy)_2Os-BiBzIm-Os(bpy)_2]^{2+}$ | 0.40 | 0.58 | 180 | [17] |
| $[(Cl)_2(bpy)Ru-bpym-Ru(bpy)(Cl)_2]$ | | | 320 | [6] |
| $[(Cl)(bpy)_2Ru-pyzc-Ru(bpy)_2]^{2+}$ | 0.93 | 1.14 | 210 | [6] |
| $[(Cl)(bpy)_2Ru-dppm-Ru(bpy)_2(Cl)]^{2+}$ | 0.92 | 1.06 | 140 | [6] |
| $[(Cl)(bpy)_2Ru-pz-Ru(bpy)_2(Cl)]^{2+}$ | 0.89 | 1.02 | 130 | [6] |
| $[(Cl)(bpy)_2Ru-pym-Ru(bpy)_2(Cl)]^{2+}$ | 0.87 | 0.99 | 120 | [6] |
| $[(Cl)(bpy)_2Ru-4,4'\text{-}bpy-Ru(bpy)_2(Cl)]^{2+}$ | 0.80 | 0.85 | 50 | [6] |
| $[(NH_3)_4Ru-bpym-Ru(NH_3)_4]^{4+}$ | 0.83 | 1.02 | 190 | [16] |
| $[(NH_3)_4Ru-dpp-Ru(NH_3)_4]^{4+}$ | 0.90 | 1.29 | 390 | [26] |
| $[(NH_3)_5Ru-pz-Ru(NH_3)_5]^{4+}$ | 0.37 | 0.76 | 390 | [6] |
| $[(CN)_4Fe-dpp-Fe(CN)_4]^{4-}$ | 0.41 | 0.56 | 150 | [16] |
| $[(CN)_4Fe-bpym-Fe(CN)_4]^{4-}$ | 0.53 | 0.67 | 140 | [16] |
| $[Ru(terpy)]_2(tpp)^{4+}$ | 1.43 | 1.72 | 290 | [26b] |
| $[Ru(tterpy)]_2(tpbp)^{2+}$ | 0.34 | 0.505 | 165 | [30] |
| $[Os(tterpy)]_2(tpbp)^{2+}$ | 0.22 | 0.34 | 120 | [30] |

is not surprising since it involves oxidation of a complex carrying 11+ charges. A similar behaviour is seen in the higher oligomer [10], $Ru\{(dpp)Ru[Ru(dpp)Ru(bpy)_2]_2\}_3{}^{20+}$. This decamer has been prepared by the reaction of the $Ru(dpp)_3{}^{2+}$ core with three $Ru[(dpp)Ru(bpy)_2]_2Cl_2{}^{4+}$ units. The complex showed a single six-electron oxidation wave corresponding to simultaneous oxidation of the six equivalent peripheral $Ru^{2+}$ ions.

Petersen examined [26b] binuclear complexes based on the tridentate bridging ligand, tetrakis(2-pyridyl)pyrazine (tpp, **30**) of the type $[\{(terpy)Ru\}_2(tpp)]^{4+}$. The difference between the first and second oxidation potential ($\Delta E$) is much higher (data given in Table 3) than what has been observed in the corresponding bidentate bridge version, $[\{(bpy)_2Ru\}_2(dpp)]^{4+}$. Table 3 also includes $\Delta E$ data for the binuclear complexes derived using another tridentate bridge, tetrapyridylbiphenyl (tpbp, **27**). In view of the strong IT bands observed in the latter complexes, they are discussed later in Section 7.

Attention must be paid to the fact that, in some of the polyimine bridging ligands, the metal chelation sites can be non-equivalent (asymmetric bridges!). In bpt, for example, the first metal uses the $N^1$ (or $N^4$) of triazole and the second one uses the $N^2$ site [20]. The charge densities at these sites are different. For this reason, the binuclear complex shows two distinct oxidation waves with a peak separation of 300 mV. In the case of the extended bpbt-bridged binuclear complex [22], chelation of the first and second $Ru(bpy)_2$ units occurs at two ends of the bridging ligand. The two chromophoric units have a significant separation distance and can be considered similar. Electrochemical studies show however two distinct waves with a $\Delta E_{1/2} \approx 160$ mV. Clearly there is substantial metal–metal interaction taking place through a delocalized system. The ligand binds to the third metal centre as a dianion and hence the third chromophore is clearly different from the first two. The mono-, bi- and trinuclear complexes of hat, $[(bpy)_2Ru]_n(hat)^{n2+}$ ($n = 1$–3) show distinct oxidation waves indicating the non-equivalence of the three metal centres [23].

### *5.1. Comproportionation*

For the binuclear complexes listed in Table 3, the comproportionation constant spans a wide range: from $>10^8$ for the azo-bis(2-pyridine) to $<10^2$ for the pz-bridged systems. For binuclear complexes with low $K_{\text{com}}$ values such as $[(\text{bpy})_2\text{Ru}]_2(\text{dpp})^{4+}$, it has not been possible to achieve quantitative conversion of [2,2] to the mixed valence [2,3] form. At concentrations $\geqslant 10^{-5}$ M, comproportionation takes place efficiently. Ernst et al. [19] addressed the question of what determines the comproportionation constant in ligand-bridged symmetric homodimers such as $[(\text{bpy})_2\text{Ru}]_2(\text{BL})^{4+}$. Using the electrochemical data of four different α-diimine bridging ligands, BL = 2,2′-bpym, 2,5-bis(2-pyridyl)pyrazine (bppz), 3,6-bis(2-pyridyl)-1,2,4,5-tetrazîne (bptz) and azobis-2-pyridine (apy), they have argued that the electron density at the coordination centres in the LUMO determines the $K_{\text{com}}$ values of the mixed valence state $\text{Ru}^{\text{II}}$–BL–$\text{Ru}^{\text{III}}$. Neither the number of mediating π-centers nor the orientation of the two metal centres plays a significant role.

### *5.2. Comparison based on mononuclear complexes*

Up till now, assessment of electronic communication was based on the difference in the first and second oxidation potentials of symmetric homobinuclear complexes. The shift in the first oxidation potential of the binuclear species with respect to the mononuclear one has also been proposed as a measure of the electronic coupling [26b]. Table 4 presents some representative data on the difference between the first oxidation potential ($\Delta E_{\text{ox}}$) of $[\text{Ru}(\text{bpy})_2]_2(\text{BL})^{4+}$ with that of the $\text{Ru}(\text{bpy})_2(\text{BL})^{2+}$, $\Delta E_{\text{red}}$ values for the first reduction and lowest energy MLCT absorption maxima for some of the binuclear complexes. In most of the cases investigated (dpp, dpq, hat, tppq, ppz, ...), the $\Delta E_{\text{ox}}$ values are very small (50–100 mV) and most of the difference arises from electrostatic/coulombic effects (oxidations rendered more difficult by the higher charge carried by the binuclear complex). These systems have been interpreted to exhibit weak metal–metal interactions. The variation in the $\Delta E$ values listed in Table 4 for various bridging ligands is much smaller than the variations in $K_{\text{com}}$ values calculated using the first and second oxidation potential of the binuclear complex (Table 3). Hence evaluations of the electronic coupling must be based solely on $\Delta E$ values of the polynuclear complexes themselves.

### *5.3. MLCT absorption and luminescence*

Table 4 also includes some representative data on the lowest energy MLCT absorption maxima in binuclear complexes, those of the parent/mononuclear complex along with shift in the oxidation, reduction potentials observed upon formation of the binuclear complex. For bridging ligands that are good π-acceptors (majority of ligands listed in Table 1 such as dpp, dpq, hat, ...), the lowest excited state in the polynuclear complexes involves CT from the metal to the π*-orbitals of the ligand (M–BL CT). In these cases, formation of the binuclear complex involves substantial lowering of the bridging ligand π*-orbitals, without much change in the first oxidation potential. These two effects lead to a red-shift in the lowest energy absorption and emission maxima. For electron-rich and those which are anion

Table 4
Redox potential differences between the first oxidation/reduction of binuclear complexes with those of mononuclear precursors and lowest energy MLCT absorption properties in fluid solution at room temperature

| Binuclear complex | $\Delta E$ (binuclear − mononuclear) | | MLCT abs. max. (nm) | |
|---|---|---|---|---|
| | Oxid. (mV) | Red. (mV) | Binuclear | Mononuclear |
| $[\text{Ru}(\text{bpy})_2]_2(\text{dpp})^{4+}$ | 50 | −400 | 525 (24800) | 468 (11000) |
| $[\text{Ru}(\text{NH}_3)_4]_2(\text{dpp})^{4+}$ | 90 | | 558 (9500) | 545 (4500) |
| $[\text{Os}(\text{bpy})_2]_2(\text{dpp})^{4+}$ | 20 | −330 | 550 (24000) | 486 (13400) |
| $[\text{Ru}(\text{bpy})_2]_2(\text{dpq})^{4+}$ | 60 | −410 | 605 (9800) | 515 (8100) |
| $[\text{Ru}(\text{bpy})_2]_2(\text{tppq})^{4+}$ | 30 | −260 | 642 (7100) | 573 (8000) |
| $[\text{Ru}(\text{bpy})_2]_2(\text{ppz})^{4+}$ | 20 | −440 | 573 (16000) | 474sh |
| $[\text{Ru}(\text{NH}_3)_4]_2(\text{bpym})^{4+}$ | 80 | | 697 (4000) | 567 (2000) |
| $[\text{Ru}(\text{bpy})_2]_2(\text{bpym})^{4+}$ | 150 | −600 | 594 (8200) | 480sh (5040) |
| $[\text{Ru}(\text{bpy})_2]_2(\text{hat})^{4+}$ | 30 | −350 | 572 (15000) | 484sh |
| $[\text{Ru}(\text{NH}_3)_5]_2(\text{pz})^{4+}$ | 80 | | 547 | 472 |
| $[\text{Ru}(\text{bpy})_2(\text{Cl})]_2(\text{pz})^{2+}$ | | | 513 | 478 |
| $[\text{Os}(\text{bpy})_2]_2(2{,}5\text{-dpp})^{4+}$ | 350 | −340 | 616 (27000) | 498 (12300) |
| $[\text{Ru}(\text{tterpy})]_2(\text{tpbp})^{2+}$ | 20 | −60 | 543 (30600) | 506 (12800) |
| $[\text{Ru}(\text{bpy})_2]_2(\text{bpt})^{3+}$ | 190 | −70 | 453 (18500) | 480 (9900) |
| $[\text{Ru}(\text{bpy})_2]_2(\text{bpbtH}_2)^{4+}$ | ⩽30 | −20 | 481 (18000) | 480 (10500) |

donors (e.g., CN, bpt, bpbt, BiIm, BiBzIm, ...), the lowest excited state involve CT from the metal to the spectator ligands such as bpy (M–bpy CT). In the case of bpt, the formation of the binuclear complex is accompanied by a blue-shift of the lowest energy CT absorption and emission.

Luminescence data are available for a number of ligand-bridged polynuclear complexes. While certain trends can be clearly observed when one compares the results obtained on polynuclear systems with those of the parent/model compounds, quantitative comparisons are difficult to make. Some of the apparent contradictions observed amongst similar systems can be due to experimental problems. Polynuclear complexes emit very weakly in the red–near-IR region and emission detection equipments must be tuned for good response up to 1000 nm. Unfortunately this does not appear to be so in a number of cases (usage of 1P28 photomultiplier, as in the study of bpym complexes by Dose and Wilson [16b] can lead to erroneous conclusions!). Varying emission quantum yields in binuclear complexes of the former type have been interpreted earlier as indicating varying degrees of electronic communication taking place through the bridging ligand. This is not a valid approach as discussed below.

The energy-gap law [34] has been shown to be operative in the luminescence of transition metal complexes. As per this law, low energy CT excited states are associated with decreased emission quantum yields (and lifetimes) due to increased occurrence of non-radiative processes. Hence it is reasonable to expect the ligand-bridged binuclear complexes with red-shifted emission to show shorter lifetime and decreased emission yields. The bi- and trinuclear complexes based on HAT show red-shifted absorption and weaker room temperature emission from the Ru–hat CT state (with respect to the mononuclear complex). The first oxidation potential is nearly identical in the mono-, bi- and trinuclear complexes. Jacquet and Kirsch-De Mesmaeker [23c] examined the temperature dependence of emission in polynuclear complexes (hat-based) to probe the possible role of the 3MC state in influencing emission properties. As has been noted earlier, multicomplexation leads to significant stabilization of the ligand $\pi^*$-orbitals without much change in the metal $d\pi$ level. If the MC state is not affected, multicomplexation should lead to a larger separation between the MLCT and MC levels.

### *5.4. Intervalence transitions*

Partially oxidized forms of the polynuclear complexes of bpt, biBzIm, biIm, bpt and bpbt show moderately intense IT bands. Table 5 presents some representative data on this available from the literature [7,8]. These anionic bridging ligands act as strong $\sigma$-donors as well as $\pi$-acceptors, stabilizing both the higher and the lower oxidation states of the metal centres. Dpp and pyrazine act largely as strong $\pi$-acceptors stabilizing the lower oxidation states. Electrochemical/chemical oxidation studies of dpp-bridged Ru or Os complexes resulted in no detectable near-IR bands attributable to IT transitions. Either the IT bands are too weak to be detectable ($\epsilon \leqslant 100$ $M^{-1}$ $cm^{-1}$) or the mixed valence complexes are chemically unstable, undergoing cleavage with time (IT transitions of pz-bridged complexes are, in general, very weak). Control experiments suggest that thermal cleavage of the complexes takes place. Luminescence coming from cleaved products can be readily seen in solutions of partially oxidized forms of the binuclear dpp-based complexes.

It was mentioned earlier that the metal–metal interaction (as monitored by the difference between the first and second oxidation potential) is rather small in the complex, $[M(bpy)_2\text{–}bpbimH_2\text{–}M(bpy)_2]^{4+}$ (M = Ru, Os). However, the partially oxidized [2,3] forms of these complexes have been reported to have moderately intense IT bands. The electronic coupling matrix element ($H_{AB}$) has been estimated to be 240–300 $cm^{-1}$ for the Ru–Ru case and 140–170 $cm^{-1}$ for the Os–Os case. Protonation of the bridge has a pronounced effect on $\Delta E$ and IT. Upon protonation, the $\Delta E$ values decrease significantly and so also does the intensity of the IT band. Data on the IT maxima and bandwidths are included in Table 5.

## 6. Weakly interacting systems (Class II) involving cyanide and chalcocyanate bridges

Recently there has been a growing number of studies devoted to polynuclear complexes based on the cyanide ligand. Scandola et al. have recently reviewed the work in this area [35]. Table 6 lists data on the difference between the first and second oxidation potentials ($\Delta E$) and intervalence transitions of the mixed form for select complexes. Substantial differences (> 0.50 V) exist in the first and second oxidation of the Ru centers in the complexes $[(CN)(bpy)_2Ru\text{–}CN\text{–}Ru(bpy)_2(CN)]^+$ and $[\{(CN)(bpy)_2Ru\text{–}CN\}_2\text{–}Ru(bpy)_2]^{2+}$. It was mentioned earlier that cyanide is an asymmetric bridging ligand. Due to the inherent better electron-donating capacity of isonitriles, the N-bonded Ru centre undergoes a more facile oxidation than the C-bonded Ru. This redox asymmetry could account for some (if not all) of the observed differences. Relatively small shifts in the MLCT bands of the partially oxidized forms suggest that the redox asymmetry contributes no more than 0.2–0.3 V. Electron delocalization clearly plays an important role in causing the difference. In the binuclear complex, $[(CO)_3(bpy)Re\text{–}CN\text{–}Re(CO)_3(bpy)]^+$, the suc-

Table 5
Data on the intervalence transitions observed in mixed valence forms of ligand-bridged complexes

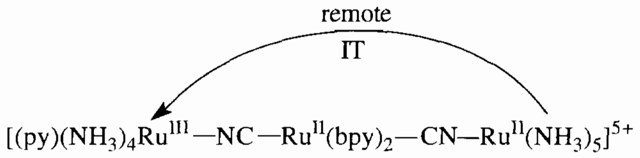
| Complex | $IT_{max}$ (nm) ($\epsilon$ ($M^{-1}$ $cm^{-1}$)) | $\Delta\nu_{1/2}$ ($cm^{-1}$) | Ref. |
|---|---|---|---|
| $[(bpy)_2Ru^{II}-BiBzIm-Ru^{III}(bpy)_2]^{3+}$ | 1950 (3400), 1062 (1300) | 2300 | [17] |
| $[(bpy)_2Ru^{II}-BiBzIm-Os^{III}(bpy)_2]^{3+}$ | 1792 (810), 1045 (1430) | 3520 | [17] |
| $[(bpy)_2Os^{II}-BiBzIm-Os^{III}(bpy)_2]^{3+}$ | 2083 (500), 1222 (1800) | 3370 | [17] |
| $[(Me_2bpy)_2Ru^{II}-BiIm-Ru^{III}(Me_2bpy)_2]^{3+}$ | 1999 (4650), 1011 (1700) | | [17] |
| $[(bpy)_2Ru^{II}-bpym-Ru^{III}(bpy)_2]^{5+}$ | ≈2000 | | [6] |
| $[(bpy)_2Ru^{II}-bpym-Os^{III}(bpy)_2]^{5+}$ | 1238 (330) | 4400 | [6] |
| $[(bpy)_2Ru^{II}-bpbim-Ru^{III}(bpy)_2]^{5+}$ | 1700 (2000) | 2520 | [6] |
| $[(bpy)_2Os^{II}-bpbim-Os^{III}(bpy)_2]^{5+}$ | 1299 (420) | 3040 | [17] |
| $[(bpy)_2Ru^{II}-bpbimH_2-Ru^{III}(bpy)_2]^{5+}$ | 1370 (<100) | 3100 | [17] |
| $[(bpy)_2Os^{II}-bpbimH_2-Os^{III}(bpy)_2]^{5+}$ | 1100 (<20) | 3020 | [17] |
| $[(bpy)_2Ru^{II}-dpimbH_2-Ru^{III}(bpy)_2]^{5+}$ | ≈1650 (≈1000) | 4340 | [17] |
| $[(bpy)_2Ru^{II}-bpt-Ru^{III}(bpy)_2]^{4+}$ | 1800 (2400) | 3300 | [20] |
| $[(bpy)_2Ru^{II}-bpt-Os^{III}(bpy)_2]^{4+}$ | 1400 (1200) | 3800 | [20] |
| $[(bpy)_2Os^{II}-bpt-Os^{III}(bpy)_2]^{4+}$ | 2000 (440), 1200 (460) | 4500 | [20] |
| $[(bpy)_2Ru^{II}-tpbq-Ru^{III}(bpy)_2]^{5+}$ | 1900 | | [18] |
| $[(bpy)_2Ru^{II}-dpq-Ru^{III}(bpy)_2]^{5+}$ | 1898 (2100) | | [21] |
| $(NH_3)_5Ru^{II}-pz-Ru^{III}(NH_3)_5$ | 1570 (5000) | 1400 | [6] |
| $(Cl)(bpy)_2Ru^{II}-pz-Ru^{III}(bpy)_2(Cl)$ | 1300 (455) | 5000 | [6] |
| $(NH_3)_5Ru^{II}-4,4'-bpy-Ru^{III}(NH_3)_5$ | 1030 (920) | | [6] |
| $(NH_3)_5Ru^{II}-bpa-Ru^{III}(NH_3)_5$ | 810 (30) | | [6] |
| $(Cl)(bpy)_2Ru^{II}-4,4'-bpy-RU^{III}(bpy)_2(Cl)$ | 985 (200) | | [6] |
| $(Cl)(bpy)_2Ru^{II}-bpa-Ru^{III}(bpy)_2(Cl)$ | 925 (150) | | [6] |

Table 6
Magnitude of the $\Delta E_{1/2}$ values for the oxidation of similar metal centres in various cyano-bridged polynuclear complexes

| Complex | $\Delta E_{1/2}$ (mV) | $IT_{max}$ (nm) ($\epsilon$ ($M^{-1}$ $cm^{-1}$)) | $\Delta\nu_{1/2}$ ($cm^{-1}$) | Ref. |
|---|---|---|---|---|
| Binuclear type | | | | |
| $[(CN)(bpy)_2Ru-CN-Ru(bpy)_2(CN)]^{+}$ | 610 | ≈1120 (7000) | ≈3500 | [7] |
| $[(Cl)(bpy)_2Ru-SCN-Ru(bpy)_2(Cl)]^{+}$ | ⩽100 | 940 (410) | 4970 | [9] |
| $[(Cl)(bpy)_2Ru-SeCN-Ru(bpy)_2(Cl)]^{+}$ | ⩽100 | 945 (450) | 5445 | [9] |
| $[(NH_3)_5Ru-NC-Ru(bpy)_2(Cl)]^{3+}$ | | 694 (3500) | 4500 | [7] |
| $[(py)(NH_3)_4Ru-NC-Ru(bpy)_2(Cl)]^{2+}$ | | 781 (3800) | 4300 | [7] |
| $[(NH_3)_5Ru^{II}-CN-Ru^{II}(NH_3)_5]^{3+}$ | | 1430 (410) | | [7] |
| Trinuclear type | | | | |
| $[\{(CN)(bpy)_2Ru-CN\}_2-Ru(bpy)_2]^{2+}$ | 270 | 1124 (9000) | 3500 | [7] |
| $[\{(CN)(bpy)_2Ru-CN\}_2-Ru(dcbpyH_2)_2]^{2+}$ | 520 | 1280 (4600) | 3500 | [8b] |
| $[\{(H_2O)(bpy)_2Ru\}_2-(NC)_2Ru(dcbpyH_2)_2]^{4+}$ | 280 | 1105 (2830) | 3140 | [8b] |
| $[\{(HO)(bpy)_2Ru\}_2-(NC)_2Ru(dcbpy)_2]^{2-}$ | 700 | 895 (1900) | 3280 | [8b] |
| $[\{(NH_3)_5Ru^{II}\}_2-(NC)_2Ru(bpy)_2]^{4+}$ | 70 | 658 (2900) | 4400 | [7] |
| $[\{(py)(NH_3)_4Ru^{II}\}_2-(NC)_2Ru(bpy)_2]^{4+}$ | 80 | 735 (3000) | 4400 | [7] |

cessive oxidation of the two Re(I) centres differ by ≈250 mV.

In the case of the trinuclear complex, the second and third oxidation correspond to the oxidation of two equivalent terminal Ru(II) sites and there is a difference of 270 mV between these two oxidations. Partially oxidized forms of the trinuclear complexes show several IT bands. Based on the results obtained from trinuclear systems, two types of IT bands can be recognized: one that involves adjacent metal centres and the other involving remote centres.



$$[(py)(NH_3)_4Ru^{III}-NC-Ru^{II}(bpy)_2-CN-Ru^{II}(NH_3)_5]^{5+}$$

The remote IT, in the above case, occurs over a large distance. Cyanide complexes show moderately intense remote IT bands ($\epsilon \geqslant 500$ $M^{-1}$ $cm^{-1}$), while hardly any remote IT can be observed in the analogous pz-bridged complexes. Hence it has been proposed [35] that these 'remote IT' involve some 'through-bond' and not 'through-space' mechanism. Electron transfer through 'superexchange' has been invoked to explain such bridging ligand dependent long distance electron transfers.

In complexes with 'aquo' spectator ligands such as $[(H_2O)(bpy)_2Ru\text{–}NC\text{–}Ru(dcbpyH_2)_2\text{–}CN\text{–}Ru(bpy)_2(H_2O)]^{4+}$, deprotonation leads to substantial changes in the oxidation potential of the corresponding Ru center. Consequently, in the mixed valence form of the deprotonated complex, its IT band blue shifts with a decrease in intensity. When the cyanide ligand is replaced by chalcogenocyanates (SCN, SeCN), the difference in the successive oxidation potentials ($\Delta E$ values) decreases substantially [9]. The intensity of the IT transitions in the mixed valence complexes also decreases significantly. A quantitative analysis of the intervalence bands of various cyano-bridged complexes yields the electronic coupling matrix element HAB $\approx 0.2\ \mu m^{-1}$ and $\alpha^2 \approx 0.03$–$0.07$. In chalcogenocyanates, $\alpha^2$ values decrease to $\leqslant 0.005$.

### 6.1. Transient formation of mixed valence species

Bignozzi et al. [7d] reported one of the first examples of excited state intervalence transfer when they monitored the transient absorption spectrum of the binuclear complex $[(NC)(bpy)_2Ru^{II}\text{–}NC\text{–}Cr^{III}(CN)_5]^{2-}$ following 347 nm laser flash excitation. The initially formed Ru-based CT excited state rapidly transfers energy to the emissive doublet excited state of Cr(III). The excited state absorption spectrum showed a visible band ($\lambda_{max} \approx 620$ nm, $\epsilon \approx 1500\ M^{-1}\ cm^{-1}$) not shown by free $Cr(CN)_6{}^{3-}$. The band was assigned to intervalence transition from Ru(II) to excited Cr(III) as shown in Eqs. (12) and (13).

$$[(NC)(bpy)_2Ru^{II*}\text{–}NC\text{–}Cr^{III}(CN)_5]^{2-} \longrightarrow [(NC)(bpy)_2Ru^{II}\text{–}NC\text{–}Cr^{III*}(CN)_5]^{2-} \quad (12)$$

$$[(NC)(bpy)_2Ru^{II}\text{–}NC\text{–}Cr^{III*}(CN)_5]^{2-} \xrightarrow{IT} [(NC)(bpy)_2Ru^{III}\text{–}NC\text{–}Cr^{II}(CN)_5]^{2-} \quad (13)$$

The transient was long-lived with a decay characteristic similar to that of the Cr doublet emission. The trinuclear complex $\{(CN)_5Cr\text{–}NC\}_2Ru(bpy)_2]^{4-}$ shows a similar transient intervalence absorption.

Recently we have observed [8b] excited state intervalence absorption during laser flash photolysis studies of the complexes $[(CO)_3(bpy)Re^{I}\text{–}NC\text{–}Ru^{II}(bpy)_2\text{–}CN\text{–}Re^{I}(CO)_3(bpy)]^{2+}$, $[(CN)(bpy)_2Ru\text{–}CN\text{–}Ru(dcbpyH_2)_2\text{–}NC\text{–}Ru(bpy)_2(CN)]^{2+}$ and $[(H_2O)(bpy)_2Ru\text{–}NC\text{–}Ru(dcbpyH_2)_2\text{–}CN\text{–}Ru(bpy)_2(H_2O)]^{4+}$. In the case of $Re^{I}\text{–}NC\text{–}Ru^{II}\text{–}CN\text{–}Re^{I}$, 530 nm laser flash excitation leads to selective excitation of the central $Ru(bpy)_2(CN)_2$ unit. Thc oxidized Ru centre has sufficient driving force to undergo intramolecular electron transfer with the nearly Re(I) centre as depicted by Eqs. (14) and (15).

$$[(CO)_3(bpy)Re^{I}\text{–}NC\text{–}Ru^{II}(bpy)_2\text{–}CN\text{–}Re^{I}(CO)_3(bpy)]^{2+} \xrightarrow{h\nu} [(CO)_3(bpy)Re^{I}\text{–}NC\text{–}Ru^{III}(bpy^{-a})(bpy)\text{–}CN\text{–}Re^{I}(CO)_3(bpy)]^{2+} \quad (14)$$

$$[(CO)_3(bpy)Re^{I}\text{–}NC\text{–}Ru^{III}(bpy^{-a})(bpy)\text{–}CN\text{–}Re^{I}(CO)_3(bpy)]^{2+} \xrightarrow{IT} [(CO)_3(bpy)Re^{I}\text{–}NC\text{–}Ru^{II}(bpy^{-a})(bpy)\text{–}CN\text{–}Re^{II}(CO)_3(bpy)]^{2+} \quad (15)$$

The mixed valence species can be detected via their IT absorption only during the lifetime of the CT excited state (lifetime of $Ru^{III}$). Matching decay kinetics of the transient absorption of the IR band (IT) with the emission decay of CT excited state is consistent with such a description. A comparison of the observed IT maxima in the excited state absorption spectra with those of the mixed valence species prepared by chemical oxidation shows that the excited state intervalence occurs at higher energies. In the excited state, the locally excited Ru complex has one of its 'bpy' ligands in the reduced state and this would lead to an increase in the energy of the associated intervalence transfer. An alternate way of stating this is that, in the excited state, the oxidation potential of the complex is low and a larger $\Delta E$ is obtained.

## 7. Cases of strongly interacting systems (Class III)

The classical Creutz–Taube mixed valence complex, $[(NH_3)_5Ru^{III}\text{–pz–}Ru^{II}(NH_3)_5]^{5+}$ has been a very intriguing one since it does not appear to fall squarely into either the predominantly valence localized Class II or to the fully delocalized Class III category. Curtis and co-workers [36] have used a novel approach to investigate the metal–metal bonding, consisting of a systematic introduction of redox asymmetry into the dimer using a *trans*-$LRu(NH_3)_4$ fragment on one end of the molecule, and L is varied over different nitrogen heterocycles so as to 'tune' the redox potential at the other end. Variations in the redox potential at the other end are then observed and their magnitude is taken as being indicative of the extent of coupling between the sites. Results clearly indicate that complexes of the Creutz–Taube type do conform to Class III while complexes such as $[(Cl)(bpy)_2Ru\text{–pz–}Ru(NH_3)_4L]^{3+}$ fall clearly under Class II.

While the metal–metal interaction is negligible in symmetric homobinuclear complexes based on back-to-back linked terpyridine, significant electronic coupling has been found in the corresponding bis-cyclometallating analogue, $tpbp^{2-}$ ($tpbpH_2$ = 3,3′,5,5′-tetrapyridylbiphenyl) [30]. The symmetric binuclear ruthenium complex, $[\{Ru(tterpy)\}_2(tpbp)]^{2+}$ (tterpy = 4′-*p*-tolyl-2,2′:6′,2″-terpyridine) undergoes two distinct one-electron oxidations with a $\Delta E_{1/2} \approx 165$ mV. The $K_c$ value of 600 is comparable to that in $[(Cl)(bpy)_2Ru$–$pz$–$Ru(bpy)_2(Cl)]$ in spite of the much larger distance between the two metal centres (11.0 Å in the case of tpbp as compared to 6.8 Å for the pyrazine case). As has been observed with other bridging ligands, the $\Delta E_{1/2}$ is slightly smaller ($\approx 120$ mV) for the corresponding bis-osmium complex $[\{Os(tterpy)\}_2(tpbp)]^{2+}$. The mixed valence complex $[(tterpy)Ru^{II}$–$(tpbp)$–$Ru^{III}(tterpy)]^{3+}$ showed a broad, intense band in the near-IR region with a maximum at 1820 nm ($\epsilon = 27\,000$ $M^{-1}$ $cm^{-1}$, $\Delta\nu_{1/2} \approx 2800$ $cm^{-1}$). The intensity of the IT band and the calculated matrix elements ($a \approx 0.15$ and 0.12 eV for the $Ru^{II}Ru^{III}$ and $Os^{II}Os^{III}$ cases, respectively) suggest extensive delocalization of charge (Class III system) is taking place through the bridging ligand. The IT band maximum is also solvent independent (1830 ± 10 nm in $CH_3CN$, acetone, DMF and DMSO) as expected for Class III systems. The $tpbp^{2-}$ bridging ligand is thus unique in exhibiting high electronic coupling over large metal–metal center separations (11 Å). Whereas the $Ru^{II}Ru^{III}$ complex shows a single band of Gaussian shape, the $Os^{II}Os^{III}$ complex shows two overlapping bands, as observed previously in other dinuclear osmium complexes where large spin–orbit coupling takes place.

In an elegant extension of the above work, Constable et al. [31] prepared the binuclear complex $[(pbpy)Ru]_2(bpqp)^{2+}$ derived with the back-to-back linked terpy ligand, bpqp and cyclometallating 6-phenyl-2,2′-bipyridine (pbpy) as a tridentate spectator ligand. The difference in redox potentials for the two $Ru^{II}/Ru^{III}$ processes ($\Delta E$) in this complex is +0.13 V, similar to +0.17 V observed for the tpbp-based complex $[(4\text{-methylphenyl-terpy})Ru]_2(tpbp)^{n+}$. In the same way the near-IR spectrum of the mixed valence complex cation exhibits an intense IT band: $\lambda_{max} = 1657$ nm with $\epsilon \approx 25\,000$–$30\,000$ $M^{-1}$ $cm^{-1}$. Clearly the effect of strong donor ligands on the IT of mixed valence complexes is more pronounced when they are present as part of the bridge than when they are present as spectator linked to one of the metal centres involved in the IT process.

## 8. Conclusions

The choice of bridging ligands available is quite extensive so that it should be possible to synthesize polynuclear complexes with the desired ('tailor-made') properties. The extent of electronic coupling in polynuclear complexes depends on a number of factors: electronic nature of the bridge, the spectator ligands and the metal centres. The difference in the first and second oxidation potential ($\Delta E$) in binuclear complexes is a good measure of the electronic communication ('coupling') between the metal centres, at least in symmetric homo systems. Intervalence transitions, if observable, is a better indicator, especially the intensity and the bandwidth of the IT bands. Complexes with bridging ligands that are electron-rich such as bpt, BiBzIm, CN (and recently cyclometallating bridges) show moderately intense IT bands. For a given bridge, the electronic coupling can be modulated significantly by spectator ligands. As discussed in the last section, cyclometallating ligands even when present as a spectator contributes strongly to the intensity of IT band in mixed valence complexes.

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