

## Modulation of internuclear communication in multinuclear

### Ruthenium(II) polypyridyl complexes

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The synthesis and characterization of dinuclear ruthenium polypyridyl complexes based on the bridging ligands 1,3-bis-(5'-(pyridin-2''-yl)-1'H-1',2',4'-triaz-3'-yl)-benzene, 1,4-bis-(5'-(pyridin-2''-yl)-1'H-1',2',4'-triaz-3'-yl)-benzene, 2,5-bis-(5'-(pyridin-2''-yl)-1'H-1',2',4'-triaz-3'-yl)-thiophene, 2,5-bis-(5'-(pyrazin-2''-yl)-1'H-1',2',4'-triaz-3'-yl)-thiophene, and of their mononuclear analogues are reported. Electrochemical studies indicate that in these systems, the ground state interaction is found to be critically dependent on the nature of the bridging ligand and its protonation state with strong and weak interactions being observed for thienyl and phenyl linked complexes respectively.

**Key words:** Ruthenium, mixed valence, LMCT, thienyl, spectroelectrochemistry

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The design and synthesis of polynuclear metal complexes containing electro- and photo-active units is of great interest because of their potential to serve as building blocks for the design of supramolecular assemblies and molecular devices<sup>1</sup>. Ruthenium(II) polypyridine complexes are playing a key role in the development of systems capable of

performing photo- and/or redox-triggered functions such as charge separation in photochemical solar energy conversion<sup>2</sup> and information storage devices<sup>3</sup>. Especially, species featuring photophysical properties and redox behaviour, which can undergo controlled modification [reversibly] by external stimuli, are of interest<sup>3,4</sup>. One area, which is of considerable interest in this respect is the control of internuclear interaction in multinuclear assemblies. The role played by the bridging ligand in determining such interaction, and in allowing manipulation of its strength by external stimulus, is well recognized<sup>5,6</sup>.

In recent years, detailed studies of binuclear complexes incorporating the 1,2,4-triazole moiety as a bridging unit (*e.g.* **1a/1b** in Figure 1) have been carried out<sup>7,8</sup>. The 1,2,4-triazolato anion can coordinate directly to two metal centres (*e.g.* **1a**)<sup>7,8</sup> or form a part of an extended bridging unit (*e.g.* **2a**)<sup>9</sup>. The photochemical and photophysical properties of several Rh(III), Ir(III), Ru(II) and Os(II) homo- and hetero-metallic complexes incorporating 1,2,4-triazole based bridging ligands have been extensively studied<sup>8,10,11</sup>. The results obtained from these studies indicate that interaction between metal centres in dinuclear complexes such as **1a** and **1b** is efficient and facilitated by a hole transfer superexchange mechanism<sup>7e</sup>. More recently, the capability of 1,2,4-triazole based bridging ligands of tuning the nature of the interaction by variation of both pH and bridging moiety, has been demonstrated in the binuclear complexes **2a**, **2b**<sup>9</sup> and **3**<sup>12</sup> (see Figure 1).

In this contribution the range of triazole based bridging ligands is expanded (*i.e.* **4**, **5** and **6a/6b**, Figure1) in an effort to understand more fully the factors, which determine

the strength of ground state interaction in this class of binuclear complex. A detailed analysis of the electronic, electrochemical and spectroelectrochemical properties of the dinuclear complexes (Figure 1) and their mononuclear analogues (Figure 2) is reported and the results are discussed in the context of earlier studies on related complexes (*i.e.* **1a/1b**, **2a/2b** and **3** in Figure 1)<sup>7-9,12</sup>.

## Results and Discussion

### *Syntheses and structural characterisation*

The synthesis and structural characterisation of **m4**, **m5**, **4** and **5** (where **m** denotes the mononuclear complex) are reported elsewhere<sup>13</sup>. Preparation and purification of the binuclear complexes **m6a**, **m6b**, **6a** and **6b** were carried out by standard procedures as described in the experimental section. The compounds are fully characterised by <sup>1</sup>H NMR spectroscopy and mass spectrometry. Of particular interest in previous studies has been the formation of coordination isomers, most notably for **2a/2b**<sup>9</sup>. For 1,2,4-triazole based complexes, both N2 and N4 nitrogen atoms of the triazole ring are available for coordination (Figure 3) resulting in, potentially, the formation of a mixture of isomers forming, *i.e.* five binuclear isomers in the case of **2a** and **2b**<sup>9</sup>. A novel synthetic approach, involving coupling of mononuclear subunits, was employed to successfully prepare **2a/2b** with complete control of the coordination mode of the complexes formed<sup>9</sup>. For **4**, **5** and **6a/6b**, however, the presence of a bulky substituent in the C5 position of the triazole ring was expected to prevent the formation of N4 bound isomers, based on previous experience with related mononuclear complexes<sup>9,14</sup> and **3**<sup>12</sup>. Hence direct reaction of the bridging ligands with *cis*-[Ru(bpy)<sub>2</sub>Cl<sub>2</sub>] should result in only one

major isomer being formed (*i.e.* where both metal centres are bound via the N2 nitrogen).

In order to confirm the coordination mode of the complexes,  $^1\text{H}$  NMR spectroscopy was employed<sup>12</sup>. Figure 4 shows the  $^1\text{H}$  NMR spectra of **6a** and its mononuclear analogue **m6a**. The only significant differences between the mononuclear and binuclear complexes arise from the proton signals due to the spacer group (*e.g.* the thienyl moiety). For **m6a** signals corresponding to the H3 (d), H4 (dd) and H5 (d) of the monosubstituted thienyl ring are observed at between 7.0 and 7.6 ppm. For **6a** a single resonance at ~7.45 ppm (2H) is observed. An additional consideration is the presence of stereoisomers. It would be expected that the binuclear complexes would exhibit twice the number of proton signals due to the presence of diastereoisomers as is the case for **1a**<sup>7d</sup>, however due to the large separation of the metal centres, no appreciable differences between the spectra of the diastereoisomers are observed. It is clear that the spectra of the mono and binuclear complexes are almost identical, confirming that the binuclear complexes are N2N2 bound, in agreement with related complexes<sup>7,8,12,15</sup>. For **4**, **5** and **6b** N2N2 coordination was confirmed by  $^1\text{H}$  NMR spectroscopy in a similar manner. For **4**, three phenyl resonances (4H) are observed confirming the meta-substitution of the phenyl spacer, whilst for the para-substituted phenyl ring of **5**, only a single phenyl resonance (4H) is found. As for **m6a**, in the mononuclear complexes **m4**, **m5** and **m6a** the loss of symmetry results in an increase in the number of bridging ligand resonances.

### *Redox properties*

Oxidation and reduction potentials of all complexes together with some related systems are presented in Table 1. Assignment of redox processes is accomplished by comparison with previously reported 1,2,4-triazole and thienyl containing complexes<sup>7-9,12,16</sup>. The waves in the anodic region of the cyclic voltammograms are assigned to metal-centred and ligand oxidations, while in the cathodic region redox waves are assigned to polypyridyl reductions<sup>23</sup>.

*Metal centred oxidation processes.* All of the mononuclear complexes exhibit a single metal centred oxidation wave with both **m6a/m6b** and their full protonated forms **Hm6a/Hm6b** exhibiting ligand based oxidation processes (*vide infra*). For the protonated complexes, an anodic shift of between 250 and 300 mV compared with the deprotonated complexes is observed and reflects the reduction in the  $\sigma$ -donor strength of the 1,2,4-triazole moiety upon protonation. For the deprotonated dinuclear complexes **4** and **5** and for all fully protonated complexes (*i.e.* **H<sub>2</sub>4**, **H<sub>2</sub>5**, **H<sub>2</sub>6a** and **H<sub>2</sub>6b**) a single bielectronic metal-based redox wave (with a  $E_{an}-E_{cat} \sim 70$  mV) is observed, in agreement with the electrochemical properties reported previously for **3**<sup>15</sup>. For the fully deprotonated binuclear complexes **6a** and **6b**, however, a separation ( $\Delta E$ ) between the first and second metal oxidation wave of approximately 100 mV is observed. This separation is close to that observed for the monoprotonated binuclear complexes **H2a** and **H2b** (Table 1)<sup>9</sup>.

In multinuclear complexes containing identical, non-interacting, centres a current-potential response having the same redox potential and shape (but increased current) as

that of the corresponding molecule containing a single centre is observed<sup>17</sup>. That no difference in the metal redox potential of the mono- and di-nuclear complexes (with the exception of **6a** and **6b**) is observed indicates electrostatic<sup>18,19</sup> and resonance stabilisation effects are small and, at most, only a small electronic coupling between the two metal centres in the ground state is present<sup>20-22</sup>. The comproportionation equilibrium constant,  $K_c$ , is directly related to the difference in the first and second metal oxidation processes ( $\Delta E$ ) and reflects the stability of the mixed valence complexes (equation 1). For **6a** and **6b**,  $K_c$  is  $\sim 60$ . For all other binuclear complexes a statistical value of 4 is assumed since the first and second metal oxidation processes are coincident<sup>23</sup>.

$$K_c = e^{\Delta E \text{ (mV)} / 25.69} \quad \text{at } T = 298 \text{ K.} \quad \text{(equation 1)}$$

*Ligand centred oxidation processes.* As expected neither **m4**, **m5**, **4** nor **5** exhibit ligand based oxidation processes<sup>7-9</sup>. For **6a/6b** and **m6a/m6b**, irreversible oxidation processes at  $\sim 1.4$ - $1.6$  V, assigned as thienyl oxidation, are observed. Assignment is based on their redox potential, irreversibility and by comparison with other thienyl containing complexes<sup>16</sup>.

*Ligand centred reduction processes.* The reduction waves observed for all the complexes have been assigned as bpy-based by comparison with structurally related complexes<sup>7,8,10</sup>. The redox waves at  $\sim -1.4$  and  $-1.65$  V are typical of bpy-based reductions. The bpy-based reductions occur at a more negative potential than their  $[M(\text{bpy})_3]^{2+}$  analogues due to the  $\sigma$ -donor properties of the 1,2,4-triazole ligands, which enhance not only the electron density at the metal centre, but also increase back-bonding

from the metal to the bpy ligands. The weak interaction of the metal units indicated by the oxidation behaviour in the dinuclear complexes is reflected in the reduction patterns observed. In all the dinuclear complexes the first peak is attributed to simultaneous one-electron reduction of a bpy ligand at each metal centre<sup>18</sup>. The electron rich nature of the thienyl moiety (as indicated by its low oxidation potential) and of the 1,2,4-triazole based ligands, being weaker  $\pi$ -acceptors than bpy, ensures that they are more difficult to reduce and these redox couples lie outside the potential window investigated. As has been found for other diimine complexes, irreversible waves corresponding to the second reduction process of the bpy ligands and desorption spikes are observed at negative potentials<sup>24,25</sup>. This situation is particularly aggravated for measurements involving the protonated complexes. As reported previously by Hage<sup>18</sup> and others, it is very difficult to obtain satisfactory reduction potentials in acidic solutions due to adsorption onto the electrode surface and deprotonation at negative potentials.

#### *Electronic and acid/base properties of Ru(II) complexes*

The UV-Vis absorption data for all complexes are shown in Table 1. The electronic absorption spectra of all complexes are dominated in the visible region by  $d\pi - \pi^*$  metal to ligand charge transfer (MLCT) transitions typical of complexes of this type<sup>7,8,27</sup> and in the UV region (250-350 nm) by intense ligand based  $\pi-\pi^*$  transitions associated with the 2,2'-bipyridyl and bridging ligands. The UV-Vis absorption spectra of the deprotonated complexes are all red-shifted with respect to  $[\text{Ru}(\text{bpy})_3]^{2+}$  as a result of strong  $\sigma$ -donor properties of the negatively charged triazole moiety. Upon protonation the triazole ring becomes a weaker  $\sigma$ -donor/stronger  $\pi$ -acceptor, resulting in an overall blue shift in the absorption spectrum. A comparison of the absorption spectra of the

mononuclear **m4/m5** and dinuclear **4/5** complexes in their protonated and deprotonated forms reveals that the energies of the absorption bands are not significantly different, with the extinction coefficients of the binuclear complexes being twice those of the mononuclear complexes (Table 1). For **6a** and **6b**, the situation is complicated by the presence of two absorption bands at ~ 360 nm and 500 nm which are absent in the spectra of **4** and **5**. These bands are likely to be due to the thienyl group and have been observed previously for terpyridine based thienyl bridged systems<sup>16</sup>. Upon protonation of the coordinated triazole rings, these absorption features are blue shifted indicating a destabilisation of the thienyl based  $\pi^*$  energy levels.

The acid dissociation constants ( $pK_a$ ) for all new complexes were determined from the change in the absorption spectra of the complexes with changing pH. For the binuclear complexes, **4**, **5** and **6a/6b** only a single protonation step is observed (Figure 5). The  $pK_a$  values of complexes (1.25 to 3.3) are found to be strongly dependent on the substituent in the C5 position, in agreement with previous studies<sup>27</sup>, with the  $pK_a$  values obtained for **m6a/m6b** and **6a/6b** being lower than for **m4**, **m5**, **4** and **5**, reflecting the electron withdrawing character of the thienyl moiety<sup>16</sup>. Similarly, the pyrazine based complex (**6b**) is more acidic than the analogous pyridine complex (**6a**), due to the greater electron withdrawing nature of the pyrazine ring<sup>27</sup>.

#### *Electronic properties of Ru(III) complexes*

The spectroscopic features of the Ru(III) complexes are summarized in Table 2. Oxidation of the mononuclear complexes results in the disappearance of the MLCT bands and the appearance of bands in the region 520-1500 nm. These new bands are



assigned as ligand-to-metal charge transfer (LMCT) bands on the basis of their energy and intensity and comparison with structurally related complexes<sup>7e,9,12</sup>. In the UV region, the characteristic splitting and shift to lower energy of the  $\pi$ - $\pi^*$  band (~280 nm) is indicative of oxidation of metal centres bound to bpy ligands<sup>28</sup>. Clear isosbestic points are obtained in all cases. For **m6a** and **m6b** oxidation results in the depletion of the absorption bands at ~ 450 nm with a concomitant growth in new bands at 425, 569 and 1049 nm. Further oxidation (at potentials above the second (thienyl oxidation wave) results in an irreversible depletion of all absorption features. For the protonated complexes similar changes were observed, with a slight blue-shift in the energy of the Ru(III) absorption features and a decrease in their intensity (*vide infra*). For the dinuclear complexes similar changes occur in the UV/Vis/Near IR spectra upon full (metal centred) oxidation. For **5**, **6a** and **6b**, however, additional bands are observed during the oxidation process (Figure 6, *vide infra*). In all compounds 100 % regeneration of the Ru(II) species was observed, confirming the reversibility of the metal oxidation process.

As can be seen in Table 2 the Ru(III) complexes show LMCT bands in the visible/near IR region of varying intensity<sup>29</sup>. With a few notable exceptions, LMCT absorption bands of Ru(III) complexes have received relatively little attention, in part due to their intensity (*e.g.*  $\epsilon \leq 500 \text{ M}^{-1}\text{cm}^{-1}$  for  $[\text{Ru}(\text{bpy})_3]^{2+}$ ) and their non-emissive nature. It has, however been found that both the energy and intensity of LMCT bands can vary greatly<sup>30</sup>, with a good correlation between the  $\sigma$ -donor strength of the ligands and band intensity. Protonation of ligands, which reduces their  $\sigma$ -donor strength, decreases the intensity of the LMCT bands and an increase in the energy of the bands in comparison

to the deprotonated complexes<sup>9,12</sup>. LMCT bands of moderate intensity in the red/near IR region have previously been observed in the mixed-ligand complexes of Ru(III) containing electron-rich donor ligands such as bisbenzimidazole<sup>31</sup> and 3,5-bis(pyridin-2'yl)-1H-1,2,4-triazole (Hbpt)<sup>7e</sup>. The position and intensity of these LMCT bands correlate well with those found here. The very intense LMCT bands for **m6a/m6b** and **6a/6b** are not, therefore, unexpected considering the electron rich nature of the thienyl group.

#### *Electronic spectroscopy of mixed valence (Ru<sup>II</sup>Ru<sup>III</sup>) complexes*

Oxidation of the binuclear complexes results in the progressive decay of the MLCT band and the concomitant grow-in of bands in the red and near-IR region of the spectrum. In the case of **5**, **6a/6b** and **H<sub>2</sub>6a/H<sub>2</sub>6b**, an additional feature appears in the near infrared region of the spectrum. Initial oxidation leads to the appearance of an absorption band between 1200 nm and 2500 nm (Figure 6 and Figure 7). As the oxidation progresses these bands decrease in intensity and more intense LMCT bands at ~1000 nm develop. Since these are very similar in energy to those found for the mononuclear parent compounds and persist in the fully oxidised species they are attributed to a charge transfer from the bridging ligand to the Ru(III) centres. The increase and subsequent decrease of the near-IR bands during the oxidation process, together with their position and intensity, strongly suggests that this absorption feature represents an intervalence transition (IT)<sup>32</sup>. However no evidence of such intervalence features can be identified for **4**. The observation that electronic coupling is not as efficient for *meta*-substituted aromatic rings has already been noted by several groups<sup>33-</sup><sup>35</sup>. The difference between **4** and **5** in terms of electronic coupling suggesting that the

interaction can be explained by a hole transfer superexchange mediated mechanism, since both complexes have similar internuclear separations and hence any through space interactions would be expected to be similar.

The extent of intercomponent interaction is of central importance in the area of supramolecular chemistry. For multinuclear systems, which exhibit metal-based redox activity, the most direct method for measuring the interaction is through electrochemical studies. Whilst  $K_c$  may in principle serve as a measure of electronic interaction between two metal sites in a binuclear complex, it is somewhat limited in identifying the true strength of the electronic delocalisation ( $\alpha^2$ ) (equation 2) and coupling ( $H_{ab}$ ) (equation 3) present. This information can be obtained spectroscopically from the IT bands observed for the mixed valence complexes using equations 2 and 3<sup>36,37</sup>.

$$\alpha^2 = \frac{(4.2 \cdot 10^{-4}) \cdot \epsilon_{\max} \cdot \Delta\nu_{1/2}}{d^2 E_{op}} \quad \text{(equation 2)}$$

$$H_{ab} = [\alpha^2 E_{op}^2]^{1/2} \quad \text{(equation 3)}$$

where  $\epsilon_{\max}$  is the maximum extinction coefficient,  $\nu_{\max}$  is the band position in  $\text{cm}^{-1}$ ,  $\Delta\nu_{1/2}$  is the band width at half maximum ( $\text{cm}^{-1}$ ) and  $d$  is the metal-metal distance in Å. [The relevant spectral parameters obtained from these equations are listed in Table 3 together with values for related complexes.]

A theoretical basis for the study of IT bands was developed by Hush<sup>38</sup> and by Robin and Day<sup>39</sup> and later by Creutz, Meyer and others<sup>40</sup>. Compared with systems of similar internuclear separation (e.g. **2a/2b**, **3**)<sup>9,12</sup>, complex e.g. **5**, **H<sub>2</sub>6a** and **H<sub>2</sub>6b** show similar coupling strength, while the deprotonated thienyl bridged complexes (**6a/6b**) show considerably increased coupling (Table 3). Upon protonation the IT band moves to higher energy and is reduced in intensity relative to the LMCT band of the fully oxidised species, indicating a reduction in the level of communication between the metal centres. It should be noted that in the case of the protonated complexes observing the IT band is very difficult as it shows considerable overlap with the much more intense LMCT band. The low energy of the LMCT band is in itself unusual and reflects the reduced energy gap between the ligand HOMO and metal ( $t_{2g}$ ) orbitals. Examination of Table 3 shows that protonation results in a reduction in the extent of electronic delocalisation ( $\alpha^2$ ) by an order of magnitude. However it should be noted that the degree of electron coupling ( $H_{ab}$ ) is only moderately reduced. For **6a** and **6b**, the interaction strength both in terms of delocalisation and coupling for both the protonated and deprotonated complexes is comparable to that of **1a** and **1b**. This increased interaction strength may be attributable to the ability of the thienyl HOMO to overlap effectively with both the 1,2,4-triazoles and the metal d-orbitals (as evidenced by the low energy of the LMCT bands) facilitating superexchange interaction<sup>16</sup>.

For binuclear complexes bridged by a single triazolato anion a strong interaction is observed both in the separation of the 1<sup>st</sup> and 2<sup>nd</sup> metal oxidation waves ( $\Delta E$ ) and in the value of  $H_{ab}$  determined from spectroscopic parameters. Separation by two triazolato anions shows a decreased level of interaction (cf. **2a/2b**). This decrease is due to

reduced orbital overlap and therefore decreased superexchange mediated interaction<sup>41</sup>. Inclusion of a phenyl spacer further increases the distance between the metal centres. The level of interaction for these systems (**4** and **5**) is much lower than would be expected on the basis of the increased distance and reflects the poor ability of phenyl groups in mediating interaction<sup>5,42</sup>. For **H<sub>2</sub>6a** and **H<sub>2</sub>6b** this manifests itself in an increase in the energy of the IT band together with a decrease in its intensity and a reduction in the value of  $\Delta E$  (see Table 3), whilst for **H<sub>2</sub>4** and **H<sub>2</sub>5** no IT bands were observed. Protonation destabilises both the ligand HOMO and metal  $t_{2g}$  orbitals of the metal centres resulting in a perturbation in the HOMO- $t_{2g}$  orbital overlap. If the mechanism of interaction is via hole transfer superexchange, then the perturbation will be manifested by a change in both  $\alpha^2$  and  $H_{ab}$ . The electronic coupling factor,  $H_{ab}$ , calculated for **5** is similar to those obtained for the dimethoxy analogue compound **3**<sup>12</sup>. On the other hand compounds, such as **1a** (Figure 1), where a more direct chemical bond between the metal centres is present the electronic coupling is considerable stronger, with a  $H_{ab}$  value of  $700 \text{ cm}^{-1}$ . Other cases showing similarly weak coupling as observed for **5** have been reported by Collin *et al.* for dinuclear Ru(II) complexes containing back-to-back bis(terpyridine) ligands linked by phenylene spacers<sup>42</sup>. It could be argued that aromatic groups do not necessarily promote a strong electronic coupling between redox centres. Kim and Lieber found that  $(\text{NH}_3)_5\text{Ru}$ - groups connected through dipyridylbenzene and dipyridylphenyl units showed very weak intervalence spectra<sup>5</sup>. Ribou and coworkers examined intervalence electron transfer in similar  $(\text{NH}_3)_5\text{Ru}$ - complexes of dipyridylpolyenes, dipyridylthiophene and dipyridylfuran and observed stronger, more defined IT transitions, than those of the phenylene group. It was suggested that due to its strong aromaticity, phenylene is unfavourable as a

mediator of intervalence electron transfer since conjugative interaction with attached units would be realized at the expense of its own aromaticity<sup>43</sup>.

Additional information as to the interaction of the metal centres can be obtained from by estimation of the theoretical peak width at half height,  $\Delta v_{1/2\text{calc}}$  using equation 4<sup>39</sup>.

$$\Delta v_{1/2\text{calc}} = [2310(E_{\text{op}} - \Delta E)]^{1/2} \quad \text{(equation 4)}$$

If the value of  $\Delta v_{1/2}$  obtained from this equation correlates well with the value found from direct measurement, the system can be described as valence localised  $\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}$  *i.e.* Type II. If the IT band is narrower, the system is better described as Type III (valence delocalised)<sup>39</sup>. On the basis of these data (Table 3) and, in particular, since  $\Delta v_{1/2}$  observed is larger than  $\Delta v_{1/2\text{calc}}$  it seems clear that the mixed valence compounds behave as type II (or valence trapped) dinuclear species. It is interesting to note that the presence of ancillary groups such as pyrazine or pyridine have little effect on the ground state electronic properties of any of the triazole bridged systems. The values of  $\Delta E$ ,  $E_{\text{op}}$  and  $\alpha^2$  values obtained for **5a** and **5b** are the same within experimental error (as found previously for **2a** and **2b**)<sup>9</sup>. This observation and the similarity of the energies of the LMCT bands observed for the mixed valence compounds indicates that LUMO of the bridging ligand plays, at best, a minor role in determining intercomponent interaction. Instead it is expected that interaction between the metal centres is taking place via a hole transfer mechanism involving the HOMO of the metal units and bridging ligand<sup>5</sup>. This is confirmed by the decrease in interaction observed upon protonation of the bridging ligand. In a hole transfer mechanism the extent of the interaction depends on

the energy-gap between the  $d\pi$  metal orbitals (metal-based HOMO) and the  $\sigma$ -orbitals of the bridge<sup>21</sup>. The spectroscopic and electrochemical data show that the ligand-based  $\sigma$ -orbitals are stabilized upon protonation, so that the energy gap between the relevant orbitals *increases*, leading to *decreased* superexchange-assisted electronic interactions.

## Conclusions

As described in the introduction, the ability to control interaction between metal centres both by external stimuli such as pH and solvent and by variation of the spacer group between metal centres is central to the development of molecular devices. One of the aims of our investigations of the last number of years has been the investigation of intercomponent interactions in dinuclear compounds based on a variety of triazole based bridging ligands. For compounds based on the different bridging ligands shown in Figure 1 it was observed that ground state interaction via hole transfer is strong for **1a/1b** but decreases with increasing metal separation. In the phenyl-bridged compounds reported here it is evident that the interaction between the metal centres is reduced considerably. The electrochemical data show that the ground state interaction is much reduced, as expected on increasing the internuclear separation, due to the increasing distance between the metal centres. In addition since the triazole rings are not coordinated to different metal centres as is observed for **1a** and **1b**, superexchange hole transfer interactions are expected to be reduced. The importance of hole transfer is further highlighted by the observation that upon protonation of the triazole rings no intervalence bands are observed for **5** and are much weaker for **6a/6b**. The behaviour of **4** is quite different, as spectroelectrochemical data do not show any evidence for the presence of an intervalence band. This indicates that apart from distance, electronic

coupling effects are important. The absence of an intervalence band is in agreement with the expected reduced electronic coupling for *meta vs para* based systems<sup>33-35</sup>. In the systems described above it is clear that the presence of a thienyl spacer allows for a dramatic increase in the distance between metal centres compared with systems such as **1a** and **1b** with only a relatively minor loss in the interaction strength. In addition in these systems the presence of moieties which allow for external manipulation of the interaction strength, make these systems much more applicable to the building of supramolecular devices.

## Experimental Methods

### Materials

All solvents used for spectroscopic measurements were of Uvasol (Merck) grade. All other reagents were HPLC grade or better. *cis*-[Ru(bpy)<sub>2</sub>Cl<sub>2</sub>].2H<sub>2</sub>O was prepared by standard procedures<sup>44</sup>. The synthesis and characterisation of **m4**, **m5**, **4** and **5** is reported elsewhere<sup>13</sup>.

### Synthetic methods

*2-(5-thiophen-2-yl-4H-[1,2,4]triazol-3-yl)-pyridine (Hpytrth)*. 4 cm<sup>3</sup> (36 mmol) of 2-thiophene acid chloride was added dropwise to a stirred solution of 4 cm<sup>3</sup> of Et<sub>3</sub>N and 3 g (22 mmol) of pyridin-2-yl amidrazone in 50 cm<sup>3</sup> of THF. The yellow suspension formed was stirred for 2 h at room temperature followed by addition of 30 cm<sup>3</sup> of ethanol. The precipitate was collected under vacuum and air-dried overnight. The yellow precipitate was heated at reflux in 30 cm<sup>3</sup> of ethylene glycol for 1 h and the solution was cooled to room temperature. 50 cm<sup>3</sup> of water was added to the thick off-



white suspension and the product filtered under vacuum and recrystallised twice from hot ethanol. Yield 2.5 g (11 mmol, 50 %). <sup>1</sup>H NMR (400 MHz) in D<sub>6</sub>-DMSO; 8.73 (1H, d, pyH6), 8.14 (1H, d, pyH3), 8.01 (1H, dd, pyH4), 7.69 (1H, d, th), 7.65 (1H, d, th), 7.55 (1H, dd, pyH5), 7.185 (1H, dd, th). (*th* = thienyl, *py* = pyridyl, *pz* = pyrazyl)

*2-(5-thiophen-2-yl-4H-[1,2,4]triazol-3-yl)-pyrazine (Hpztrth)*. As for Hpytrth except: 3 g (22 mmol) of pyrazin-2-yl amidrazone. Yield 1.15 g (5 mmol, 22 %). <sup>1</sup>H NMR (400 MHz) in D<sub>6</sub>-DMSO; 9.29 (1H, d, pzH3), 8.77 (1H, d, pzH5), 8.76 (1H, dd, pzH6), 7.74 (1H, d, th), 7.69 (1H, d, th), 7.21 (1H, dd, th)

*2,5-bis-(5'-(pyridin-2''-yl)-1'H-1',2',4'-triaz-3'-yl)-thiophene ((Hpytr)<sub>2</sub>th)*. As for Hpytrth except: 2,5-thiophene-diacylchloride (prepared by heating at reflux 1.5 g (8.7 mmol) of 2,5-dicarboxy-thiophene in 30 cm<sup>3</sup> of SOCl<sub>2</sub>) was reacted with 3 g (22 mmol) of pyridin-2-yl amidrazone. Yield 674 mg (1.8 mmol, 21 %). <sup>1</sup>H NMR (400 MHz) in D<sub>6</sub>-DMSO; 8.74 (1H, d, pyH6), 8.17 (1H, d, pyH3), 8.06 (1H, dd, pyH4), 7.73 (1H, s, th), 7.57 (1H, dd, pyH5)

*2,5-bis-(5'-(pyrazin-2''-yl)-1'H-1',2',4'-triaz-3'-yl)-thiophene ((Hpztr)<sub>2</sub>th)*. As for Pytrth except: 2,5-thiophene-diacylchloride (prepared by heating at reflux 1.2 g (6 mmol) of 2,5-dicarboxy-thiophene in 30 cm<sup>3</sup> of SOCl<sub>2</sub>) was reacted with 2.4 g (18 mmol) of pyazin-2-yl amidrazone. Yield 334 mg (0.9 mmol, 15 %). <sup>1</sup>H NMR (400 MHz) in D<sub>6</sub>-DMSO; 9.30 (1H, d, pzH3), 8.775 (1H, d, pzH5), 8.765 (1H, dd, pzH6), 7.61 (1H, d, th)

*[Ru(bpy)<sub>2</sub>(pytrth)](PF<sub>6</sub>).H<sub>2</sub>O (m6a)*. 230 mg (0.44 mmol) of *cis*-[Ru(bpy)<sub>2</sub>Cl<sub>2</sub>].2H<sub>2</sub>O and 130 mg (0.57 mmol) of Hpytrth were heated at reflux for 8 h in 50 cm<sup>3</sup> ethanol/water (50/50 v/v). The reaction was evaporated to dryness and redissolved in the minimum of water and filtered to remove unreacted ligand. 3 drops of concentrated NH<sub>4</sub>OH<sub>aq</sub> and 2 cm<sup>3</sup> of saturated ammonium hexafluorophosphate were added to the filtrate and the precipitate collected under vacuum and air-dried. Purification by column chromatography on neutral alumina (CH<sub>3</sub>CN as eluent) yielded a single red fraction. Solvent was removed *in vacuo* and the precipitate recrystallised from methanol/water. Yield 240 mg (0.31 mmol, 70 %). Mass spec. 640.9 m/z (calc. for RuC<sub>31</sub>H<sub>23</sub>N<sub>8</sub>S M<sup>+</sup> = 641). <sup>1</sup>H NMR in CD<sub>3</sub>CN; 8.48 (1H,d), 8.46 (1H,d), 8.42 (2H, d), 8.10 (1H, d), 8.015 (1H, dd), 7.98 (1H, dd), 7.93 (4H, m), 7.86 (2H, m), 7.79 (1H, d), 7.51 (1H, d), 7.4 (4H, m), 7.31 (1H, dd), 7.26 (1H, d), 7.15 (1H, dd), 7.03 (1H, dd). CHN analysis: % found (% calc. for RuC<sub>31</sub>H<sub>23</sub>N<sub>8</sub>SPF<sub>6</sub>.H<sub>2</sub>O); C 46.32 % (46.33 %), H 2.84 % (2.99 %), N 13.80 % (13.95 %).

*[Ru(bpy)<sub>2</sub>(pztrth)](PF<sub>6</sub>).2H<sub>2</sub>O (m6b)*. As for [Ru(bpy)<sub>2</sub>(pytrth)](PF<sub>6</sub>) except 230 mg (0.44 mmol) of *cis*-[Ru(bpy)<sub>2</sub>Cl<sub>2</sub>].2H<sub>2</sub>O and 130 mg (0.56 mmol) of Hpztrth were used. Yield 200 mg (0.25 mmol, 57 %). Mass spec. 641.9 m/z (calc. for RuC<sub>30</sub>H<sub>22</sub>N<sub>9</sub>S M<sup>+</sup> = 642). <sup>1</sup>H NMR in CD<sub>3</sub>CN; 9.23 (1H, d), 8.5 (4H, m), 8.25 (1H, d), 8.01 (4H, m), 7.93 (1H, d), 7.86 (1H, d), 7.80 (2H, dd), 7.59 (1H, d), 7.40 (5H, m), 7.31 (1H, d), 7.05 (1H, dd). CHN analysis: % found (% calc. for RuC<sub>30</sub>H<sub>22</sub>N<sub>9</sub>SPF<sub>6</sub>.2H<sub>2</sub>O); C 43.60 % (43.80 %), H 2.73 % (2.92 %), N 14.97 % (15.33 %).

$[(Ru(bpy)_2)_2((pytr)_2th)](PF_6)_2 \cdot 6H_2O$  (**6a**) As for  $[Ru(bpy)_2(pytrth)](PF_6)$  except 300 mg (0.58 mmol) of *cis*- $[Ru(bpy)_2Cl_2] \cdot 2H_2O$  and 100 mg (0.27 mmol) of  $H_2(pytr)_2th$  were heated at reflux in ethylene glycol/water (3/1 v/v). Yield 150 mg (0.09 mmol, 36 %). Mass spec. 599 m/z (calc. for  $Ru_2C_{58}H_{42}N_{16}S M^{2+} = 599$ ).  $^1H$  NMR in  $CD_3CN$ ; 8.3 (8H, m), 7.90 (2H, d), 7.8 (9H, m), 7.74 (2H, d), 7.7 (5H, m), 7.62 (2H, d), 7.33 (2H, d), 7.24 (6H, m), 7.15 (2H, dd), 7.08 (2H, s), 6.97 (2H, dd). CHN analysis: % found (% calc. for  $Ru_2C_{58}H_{42}N_{16}SP_2F_{12} \cdot 6H_2O$ ); C 43.80 % (43.66 %), H 2.77 % (3.01%), N 13.68 % (14.05 %).

$[(Ru(bpy)_2)_2((pztr)_2th)](PF_6)_2$  (**6b**). As for  $[Ru(bpy)_2(pytrth)](PF_6)$  except 290 mg (0.56 mmol) of *cis*- $[Ru(bpy)_2Cl_2] \cdot 2H_2O$  and 90 mg (0.24 mmol) of  $H_2(pztr)_2th$  were heated at reflux in 25 cm<sup>3</sup> ethylene glycol/water (3/1 v/v). Yield 120 mg (0.085 mmole, 33 %). Mass spec. 600 m/z (calc. for  $Ru_2C_{56}H_{40}N_{18}S M^{2+} = 600$ ).  $^1H$  NMR in  $CD_3CN$ ; 9.28 (2H, d), 8.5 (8H, m), 8.27 (2H, d), 8.01 (8H, m), 7.91 (2H, d), 7.80 (2H, m), 7.76 (4H, d), 7.62 (2H, d), 7.40 (8H, m).

## Instrumentation

$^1H$  NMR spectra were recorded on a Bruker AC400 (400 MHz) NMR Spectrometer. All measurements were carried out in  $[D_6]DMSO$  or  $[D_1]chloroform$  for ligands  $[D_6]acetonitrile$  for complexes. Peak positions are relative to residual solvent peaks. - UV/Vis absorption spectra (accuracy  $\pm 2$  nm) were recorded on a Shimadzu UV/Vis-NIR 3100 spectrophotometer interfaced with an Elonex PC466 using UV/Vis data manager. Absorption maxima,  $\pm 2$  nm Molar absorption coefficients are  $\pm 10\%$  - pH titrations were carried out in Britton-Robinson buffer (0.04 M  $H_3BO_3$ , 0.04 M  $H_3PO_4$ ,

0.04 M CH<sub>3</sub>CO<sub>2</sub>H) (pH was adjusted using concentrated sulphuric acid or sodium hydroxide solution).

Mass spectra were obtained using a Bruker-Esquire LC\_00050 electrospray ionization mass spectrometer at positive polarity with cap-exit voltage of 167 V. Spectra were recorded in the scan range of 50-2200 m/z with an acquisition time of between 300 and 900  $\mu$ s and a potential of between 30 and 70 V. Each spectrum was recorded by summation of 20 scans.

Elemental analysis has been carried out at the Micro-analytical Laboratory at University College Dublin.

Electrochemical measurements were carried out on a Model 660 Electrochemical Workstation (CH Instruments). Typical complex concentrations were 0.5 to 1 mM in anhydrous acetonitrile containing 0.1 M tetraethylammonium perchlorate (TEAP). A Teflon shrouded glassy carbon working electrode, a Pt wire auxiliary electrode and SCE reference electrode were employed. Solutions for reduction measurements were deoxygenated by purging with N<sub>2</sub> or Ar gas for 15 min prior to the measurement. Measurements were made in the range of -2.0 to 2.0 V (vs SCE electrode). Protonation of complexes was achieved by addition of trifluoroacetic acid (0.1 M in acetonitrile) to the electrolyte solution. Cyclic voltammetry were obtained at sweep rates of 100 mV s<sup>-1</sup>; differential pulse voltammetry (DPV) experiments were performed with a scan rate of 20 mV s<sup>-1</sup>, a pulse height of 75 mV, and a duration of 40 ms. For reversible processes the half-wave potential values are reported; identical values are obtained from DPV and

CV measurements. Redox potentials are +/- 10 mV. Spectroelectrochemistry was carried out using an OTTLE setup comprising of a homemade Pyrex glass, thin layer cell (2 mm). The optically transparent working electrode was made from platinum-rhodium gauze, a platinum wire counter electrode, and the reference electrode was a pseudo Ag/AgCl reference electrode. The working electrode was held at the required potential throughout the measurement using an EG&G PAR Model 362 potentiostat. Absorption spectra were recorded as described above. Protonation of complexes under bulk electrolysis was achieved by addition of dry trifluoroacetic acid (0.1 M in acetonitrile).

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	Ru <sup>II</sup> /Ru <sup>III</sup> oxid. (in V) {ligand oxid.}	Ligand red. (in V vs. SCE)	Abs. $\lambda_{\max}$ /nm (log $\epsilon$ )	pK <sub>a</sub>	ref
<b>1a</b>	1.04, 1.34	-1.40, 1.62, -1.67	452	-	7
<b>1b</b>	1.16, 1.46	-1.26, -1.39, -1.55, -1.63	449	-	7
<b>2a</b>	0.80, 0.98	-1.46, -1.72	480	1.1, 3.8	9b
<b>2b</b>	0.92, 1.09	-1.42, -1.65	455	-	9b
<b>3</b>	0.82 (1.20, 1.40)	-1.48, -1.73	481 (4.27)	4.1	12
<b>4</b>	0.84	-1.40, -1.69	482 (2.00)	3.5	-
<b>5</b>	0.84	-1.50, -1.71 (irr)	481 (2.03)	3.6	-
<b>6a</b>	0.78, 0.87 (1.45 irr)	-1.44, -1.67	360 (4.6), 430 (4.23)	2.50	-
<b>6b</b>	0.85, 0.95 (1.41 irr)	-1.49, -1.70	344 (4.33), 438 (4.19), 510 (sh)	1.25	-
<b>m4</b>	0.84	-1.45, -1.60	482 (0.85)	3.3	-
<b>m5</b>	0.84	-1.45, -1.61	482 (0.98)	3.6	-
<b>m6a</b>	0.86 (1.62 irr)	-1.36, -1.67	480 (3.93)	3.05	-
<b>m6b</b>	0.95 (1.55 irr)	-1.43, -1.65	455 (4.15)	2.15	-
<b>H2a</b>	1.06, 1.17	-	440 (4.45)	-	-
<b>H2b</b>	1.09, 1.15	-	436	-	-
<b>H<sub>2</sub>2a</b>	1.10	-	430	-	9b
<b>H<sub>2</sub>2b</b>	1.13	-	430	-	9b
<b>H<sub>2</sub>3</b>	1.25 (1.5)	-1.49, -1.73	412 (log 28.3)	-	12
<b>H<sub>2</sub>4</b>	1.18	-1.53	440	-	-
<b>H<sub>2</sub>5</b>	1.14	-1.52, -1.79 (irr)	420	-	-
<b>H<sub>2</sub>6a</b>	1.08 (1.45 irr)	<i>not measured</i>	417 (4.45)	-	-
<b>H<sub>2</sub>6b</b>	1.18 (1.58 irr)	<i>not measured</i>	428, 515(sh)	-	-
<b>Hm4</b>	1.18	-1.47	440	-	-
<b>Hm5</b>	1.15	-1.47	432	-	-
<b>Hm6a</b>	1.19 (1.67 irr)	-	439 (4.03)	-	-

<b>Hm6b</b>	1.23 (1.55 irr)	-	438 (4.18)	-	-
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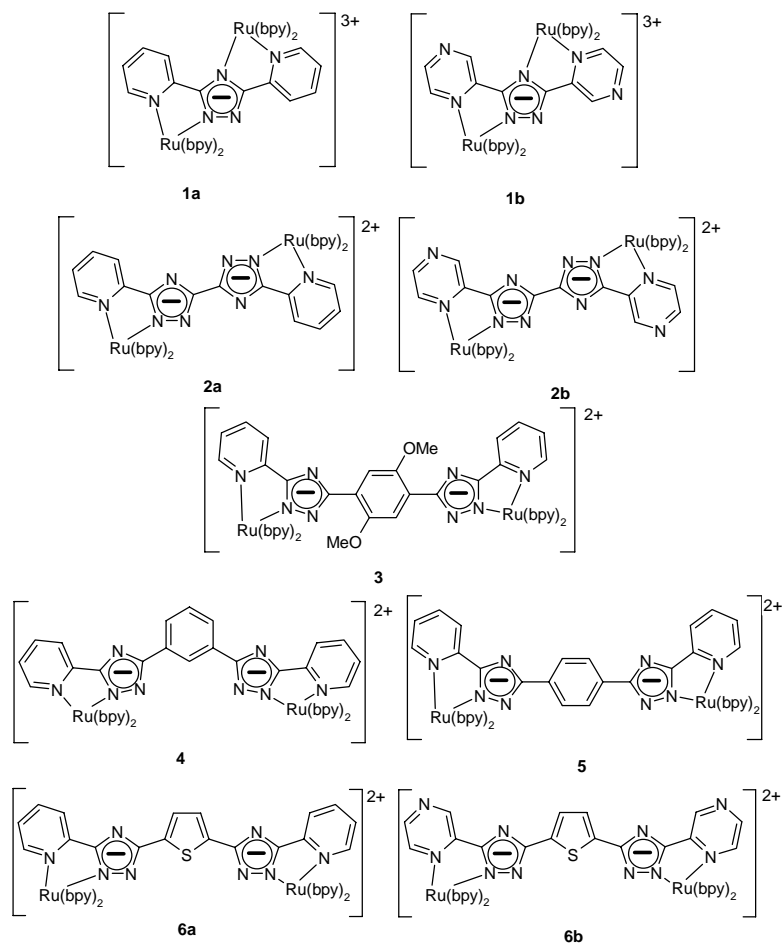
**Table 1** Electronic properties of mono- and bi-nuclear thienyl containing complexes (in CH<sub>3</sub>CN). pK<sub>a</sub> data for complexes was determined in Britton-Robinson Buffer

**Table 2** UV/Vis/NIR absorption data of the fully oxidized ruthenium complexes. All measurements carried out using CH<sub>3</sub>CN with 0.1 M TEAP.

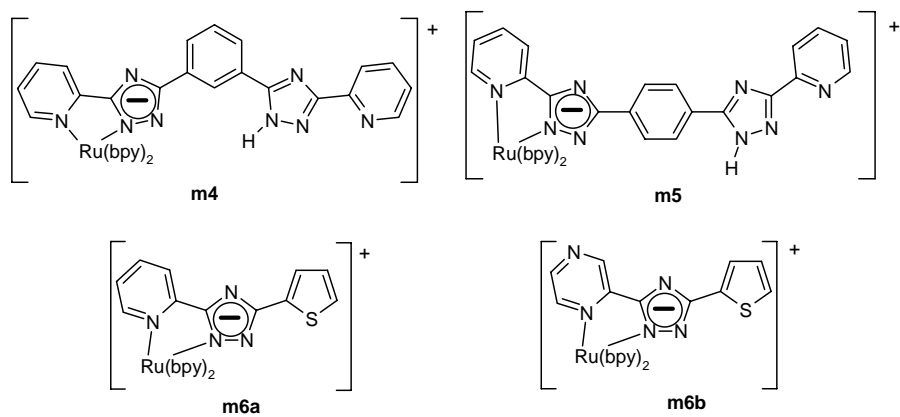
Abs. λ <sub>max</sub> / nm		Ref	
<b>1a</b>	725	<b>1b</b>	7
<b>2a</b>	570, 910	<b>2b</b>	570, 910 9b
<b>H2a</b>	560, 895	<b>H2b</b>	560, 895 9b
<b>H<sub>2</sub>2a</b>	430, 795	<b>H<sub>2</sub>2b</b>	430, 795 9b
<b>3</b>	1216	<b>H<sub>2</sub>3</b>	840 12
<b>m4</b>	530, 923	<b>Hm4</b>	520, 850 -
<b>4</b>	525, 927	<b>H4</b>	500, 755 -
<b>m5</b>	578, 978	<b>Hm5</b>	550, 900 -
<b>5</b>	535, 998	<b>H5</b>	537, 870 -
<b>m6a</b>	570, 1050	<b>Hm6a</b>	990 -
<b>6a</b>	675, 1310	<b>H6a</b>	645, 1270 -
<b>m6b</b>	570, 1060	<b>Hm6b</b>	950 -
<b>6b</b>	675, 1320	<b>H6b</b>	640, 1265 -

	$H_{ab}$ ( $\text{cm}^{-1}$ )	$\alpha^2$	$\Delta E$ (mV) $\pm 10$ mV	$K_c$	$d$ ( $\text{\AA}$ ) <sup>a</sup>	$\Delta v_{1/2\text{calc}}$ ( $\text{cm}^{-1}$ )	$\Delta v_{1/2}$ ( $\text{cm}^{-1}$ ) <sup>b</sup>	$\epsilon_{\text{max}}$ ( $\text{M}^{-1}\text{cm}^{-1}$ ) $\pm 20\%$ <sup>c</sup>	$E_{\text{op}}$ ( $\text{cm}^{-1}$ ) $\pm 100$ $\text{cm}^{-1}$	Ref
<b>1a</b>	700	0.016	300	117,910	6.5	2690	3300	2400	5556	7
<b>1b</b>	745	0.019	300	117,910	6.5	2625	4200	2200	5405	7
<b>2a</b>	459	0.007	180	1,100	9.5	3060	4690	1820	5490	9b
<b>2b</b>	352	0.004	170	750	9.5	3120	4360	1120	5580	9b
<b>5</b>	295	0.0014	0	4	12	-	4262	1040	7870	-
<b>3</b>	480	0.0055	0	4	12	-	5100	>2400	6470	12
<b>6a</b>	577	0.0102	110	72	11.5	3340	4572	5000	5720	-
<b>6b</b>	565	0.0105	100	50	11.5	3300	4520	5000	5530	-
<b>H2a</b>	435	0.0025	110	72	9.5	4250	5600	1000	8700	9b
<b>H2b</b>	425	0.0025	60	10	9.5	4300	5300	1000	8500	9b
<b>H<sub>2</sub>6a</b>	444	0.0028	0	4	11.5	-	3430	2600	8400	-
<b>H<sub>2</sub>6b</b>	430	0.0026	0	4	11.5	-	3400	2600	8450	-

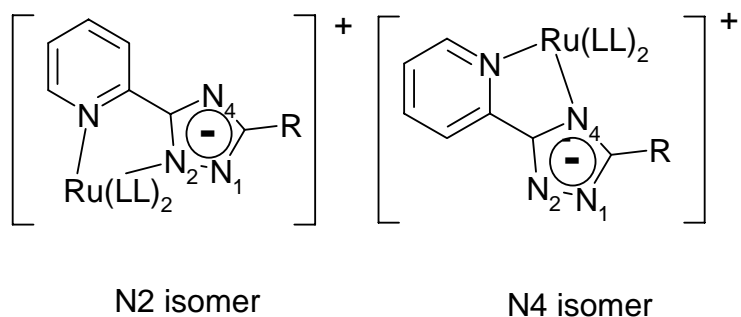
**Table 3** Spectroelectrochemical data, (a) where X-ray structure data are unavailable, d has been estimated from non-optimised Hyperchem molecular modelling (b) taken as double the width at half maximum of the high energy side of the absorption band (c) For complexes with a value of  $K_c \sim 4$  the value of  $\epsilon_{\text{max}}$  is adjusted to account for concentration<sup>44,45</sup>.



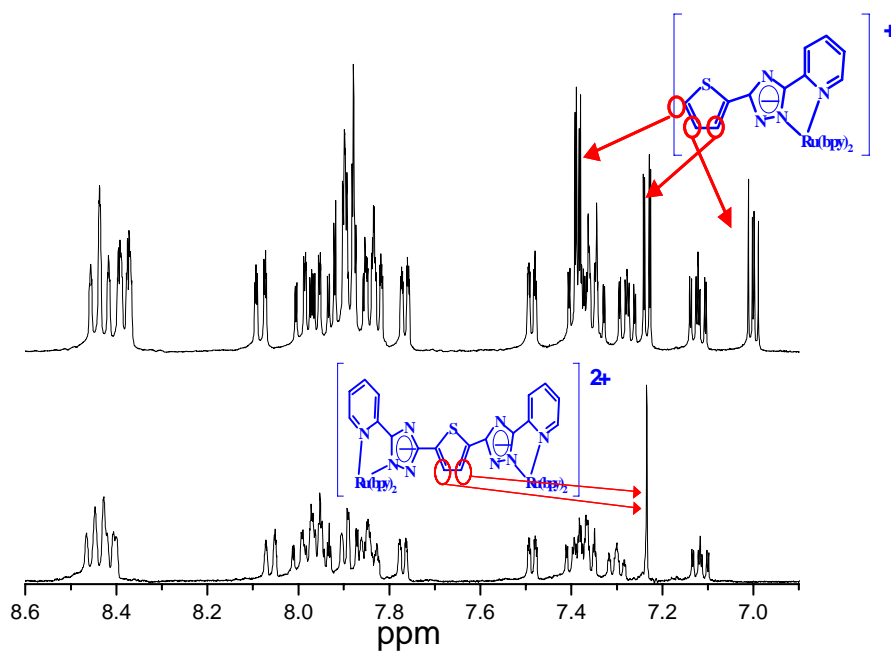
**Figure 1** Binuclear ruthenium complexes of triazole based bridging ligands



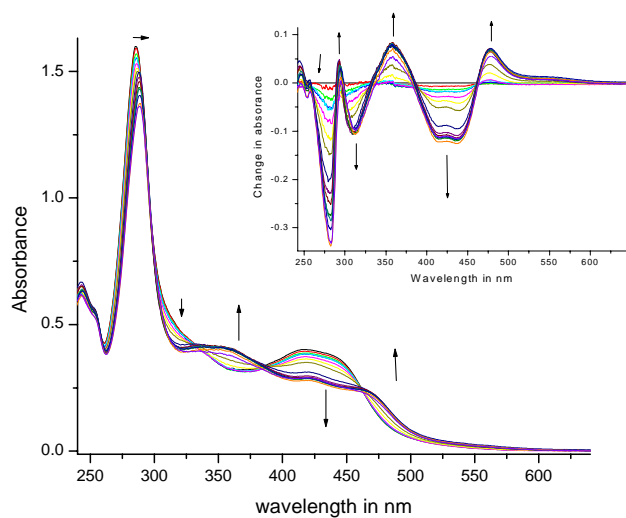
**Figure 2** Mononuclear ruthenium complexes of triazole based bridging ligands



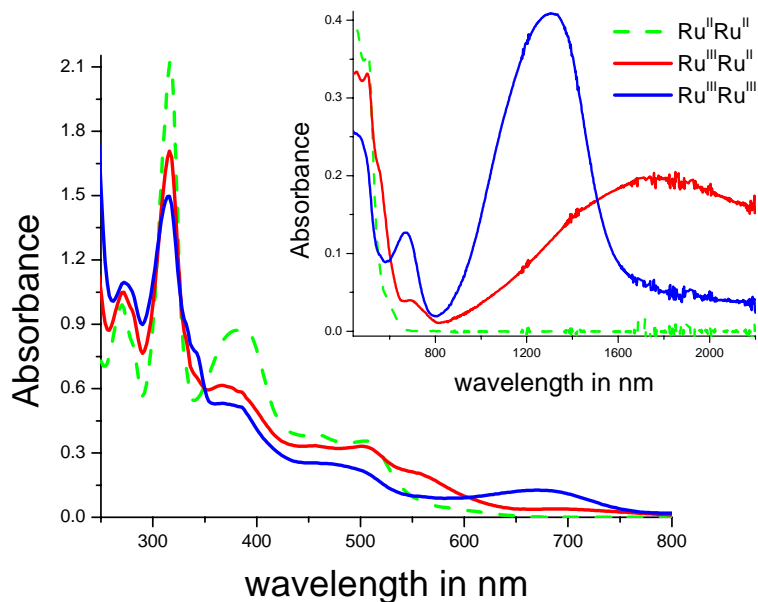
**Figure 3** N2 and N4 coordination mode



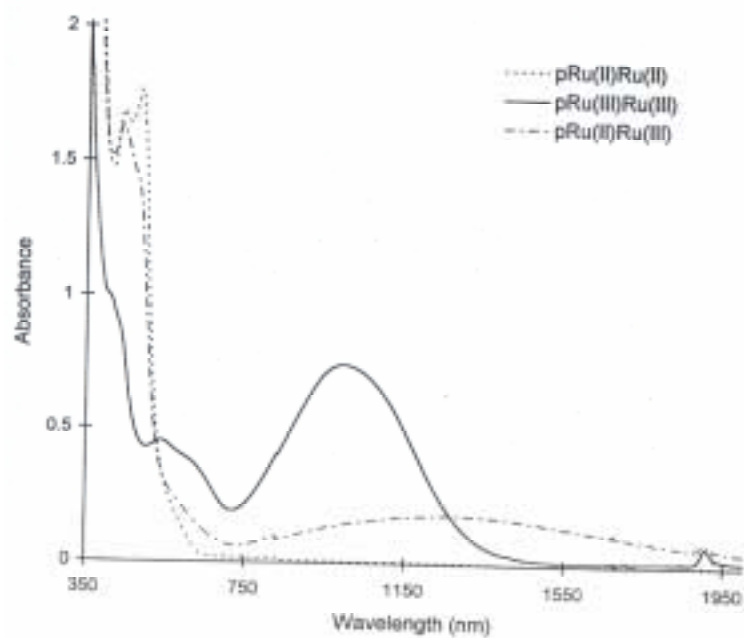
**Figure 4** <sup>1</sup>H NMR spectra of **6a** (lower) and **m6a** (upper) in CD<sub>3</sub>CN



**Figure 5** Changes in UV-vis spectra of **6b** between pH 0.5 and 10. (inset differences spectra compared with completely the protonated complexes)



**Figure 6** Changes in UV-Vis-NIR absorption spectrum of **6a** upon successive addition of 1 equivalents of  $Ce^{4+}$ . (inset shows Near-IR region)



**Figure 7** Visible/Near-IR Absorption Spectra of **5** in the  $Ru^{II}Ru^{II}$ ,  $Ru^{III}Ru^{II}$ , and  $Ru^{III}Ru^{III}$  oxidation states



*Graphical Abstract*

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Modulation of internuclear communication in multinuclear Ruthenium(II) polypyridyl

complexes

