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Ground vs. excited state interaction in ruthenium-thienyl dyads: implications for through bond interactions in multicomponent systems

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Abstract

The vibrational and photophysical properties of mononuclear ruthenium(II) and ruthenium(III) polypyridyl complexes based on the ligands 2-(5'-(pyridin-2''-yl)-1'H-1',2',4'-triaz-3'-yl)-thiophene, 2-(5'-(pyrazin-2''-yl)-1'H-1',2',4'-triaz-3'-yl)-thiophene, are reported. The effect of the introduction of the non-innocent thiophene group on the properties of the triazole based ruthenium(II) complex is examined. The pH sensitive 1,2,4-triazole group, although influenced by the electron withdrawing nature of the thiophene group, does not facilitate excited state interaction of the thiophene and Ru(II) centre. Deuteration and DFT calculations are employed to enable a deeper understanding of the interaction between the two redox-active centres and rationalise the difference between the extent of ground and excited state interaction in this simple dyad. The results obtained provide considerable evidence in support of earlier studies examining differences in ground and excited state interaction in multinuclear thiophene-bridged systems, in particular with respect to HOMO- and LUMO- mediated superexchange interaction processes.

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1. Introduction

The well-defined spectroscopic, photophysical, photochemical, and electrochemical properties of Ruthenium(II) polypyridyl complexes underlie their potential as building blocks in supramolecular assemblies. Of particular interest is their incorporation into the design of multinuclear structures capable of directing and modulating electron and energy transfer processes [1]. The ability to tune the excited state properties of these complexes is key to their potential for practical applications. Central to the development of photonic devices based on multicomponent systems is a detailed understanding of the nature of interaction

between molecular components. In the present work the differences in the extent of interaction of molecular components, in the ground electronic state and in the thexi (thermally equilibrated excited) state, are investigated.

In previous studies of dinuclear Ru(II) complexes which incorporate 1,2,4-triazole ligands in the bridging unit, the importance of the triazole bridge in mediating electron and energy transfer was demonstrated in the pH dependence of the interaction strength. In these systems a relatively strong ground state interaction between the metal centres was effective over considerable distances (typically, ~ 12 Å), whilst excited state interaction was found to be much weaker [2]. While the ground state interaction is very sensitive to the nature of the bridging unit, it appears that the excited state interaction is predominantly a through space (Förster) interaction [3].

To investigate further the ability of the 1,2,4-triazole to permit effective control over intercomponent communication, we have extended our study to include 'dyads' based

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Fig. 1. Structure of complexes and ligands.

on the ligands 2-(5'-(pyridin-2''-yl)-1'-H-1',2',4'-triaz-3'-yl)-thiophene (Hpytrth) and 2-(5'-(pyrazin-2''-yl)-1'-H-1',2',4'-triaz-3'-yl)-thiophene (Hpztrth). The electrochemical and spectroelectrochemical properties of these complexes have been reported in an earlier contribution [2], together with the properties of the non-substituted monomers and the dimeric complexes in which thiophene bridges between two Ru(II)-triazole units (see Fig. 1). In the present investigation the mononuclear complexes and their deuteriated isotopologues based on these ligands have been examined by Raman, electronic and emission spectroscopy both in the Ru(II) and Ru(III) oxidation states. The experimental data are supplemented by DFT calculations. The results obtained are compared with our earlier studies on related mononuclear complexes and on the thiophene/triazole-bridged dinuclear complexes (**5** and **6**), with particular reference to the degree of interaction between the ruthenium(II) triazole and the thienyl moieties in the ground and the excited states.

2. Experimental

2.1. Materials

All solvents employed were of HPLC grade or better and used as received unless otherwise stated. For all spectroscopic measurements Uvasol (Merck) grade solvents were employed. All reagents employed in synthetic procedures were of reagent grade or better. [Ru([D₈]-bpy)₂Cl₂] was obtained from Complex Solutions (Dublin, Ireland) and used as received. The complexes [Ru([H₈]-bpy)₂(pytrth)]PF₆ (**1a**) and [Ru([H₈]-bpy)₂(pztrth)]PF₆ (**2a**) were available from earlier studies [2]. [Ru([D₈]-bpy)₂(pytrth)]PF₆ (**1b**) and [Ru([D₈]-bpy)₂(pztrth)]PF₆ (**2b**) were prepared by similar procedures to **1a** and **2a** respectively. Deuteriation was >99.5% by ¹H NMR (see Fig. S1, supplementary information).

2.2. Physical measurements

NMR spectra were recorded on a Bruker Avance 400 (400 MHz) NMR Spectrometer. All measurements were carried out in [D₃]-acetonitrile for complexes. Peak positions are relative to residual solvent peaks. UV/Vis absorption spectra (accuracy ±2 nm) were recorded in 10 mm quartz cuvettes on a Shimadzu UV/Vis-NIR 3100 spectrophotometer interfaced with an Elonex PC466 using UV/Vis data manager. Molar absorption coefficients are ±10%. Emission spectra (accuracy ±5 nm) were recorded at 298 K using a LS50B luminescence spectrophotometer, equipped with a red sensitive Hamamatsu R928 PMT detector, interfaced with an Elonex PC466 employing Perkin-Elmer FL WinLab custom built software. Emission and excitation slit widths were 10 nm. Emission spectra are uncorrected for photomultiplier response. pH titrations of **1** and **2** were carried out in Britton-Robinson buffer (0.04 M H₃BO₃, 0.04 M H₃PO₄, 0.04 M CH₃CO₂H) (pH was adjusted using concentrated sulfuric acid or sodium hydroxide solution) and followed by monitoring the pH dependence of absorption and emission spectra. pH_i refers to the inflection point of the emission titration curve. The appropriate isosbestic point from the absorption spectra was used as the excitation wavelength for emission titrations. Luminescence lifetime measurements were made using an Edinburgh Analytical Instruments (EAI) Time-Correlated Single-Photon Counting apparatus (TCSPC) as described previously [4]. Samples were deoxygenated by bubbling for 20 min using Ar gas before measurements were carried out, followed by periodic de-aeration to maintain oxygen exclusion. Emission lifetimes were calculated using a single exponential fitting function, involving a Levenberg-Marquardt algorithm with iterative deconvolution (Edinburgh instruments F900 software) and are ±10%. The χ² and residual plots were used to judge the quality of the fits.

Ground state resonance Raman spectra of the complexes were recorded at 457.9, 488 and 514.5 nm using an Argon ion laser (Spectra Physics model 2050) as the excitation source

[5]. The laser power at the sample was typically 30–40 mW. The Raman backscatter was focused onto the entrance slit of a single stage spectrograph (JY Horiba HR640), which was coupled to a CCD detector (Andor Technology DV420-OE). Spectra generated at an excitation wavelength of 532 nm were recorded using an Andor Technology Raman Station. The spectra were run in quartz cuvettes. Solid state spectra at 785 nm were obtained on a JY Horiba Labram HR800 Raman microscope with a 300 groove grating. Transient resonance Raman spectra were recorded using the single-colour pump and probe method in which the leading edge of the pulse excites the molecules and the trailing edge probes the resultant Raman scattering [6]. The excitation source was a pulsed laser (Spectra Physics Q-switched Nd:YAG, GCR-3) at 354.7 nm with a typical pulse energy of approx 3 mJ at the sample. The Raman backscatter was focused onto the entrance slit of a double-stage spectrograph (Spex 1870), which was coupled to an ICCD (Andor Technology DH501). Typically, spectra were collected as a summation of 6000 accumulations.

2.3. Density functional theory calculations

Density functional calculations were carried out with Gaussian 03W [7] using Becke's three-parameter hybrid functional [8] with the LYP correlation functional [9] (B3LYP). The LanL2DZ basis set was used. This uses the Dunning–Huzinaga double- ζ basis functions [10] (DZ) for carbon, nitrogen, and hydrogen atoms, the Los Alamos effective core potential for the Ru core electrons, and DZ functions for the Ru valence electrons [11]. An ultrafine integration grid was used. Raman frequency calculations were carried out at the optimised geometry. GaussSum 0.8 [12] was used to calculate group contributions to the molecular orbitals and to prepare the partial density of states (PDOS) spectra. The contribution of a group to a molecular orbital was calculated using Mulliken population analysis. The PDOS spectra were created by convoluting

the molecular orbital information with Gaussian curves of unit height and FWHM of 0.3 eV.

3. Results

The visible absorption and emission data for complexes **1a/1b** and **2a/2b** are listed in Table 1, with data for related complexes included for comparison. The lowest energy absorption feature for all complexes is assigned to several overlapping singlet metal-to-ligand-charge-transfer ($^1\text{MLCT}$) transitions ($\log \epsilon \sim 4.2$), by comparison with other ruthenium polypyridyl complexes and on the basis of resonance Raman analysis (vide infra) [13]. All compounds show strong absorptions ($\log \epsilon \sim 5$) at ~ 280 nm, which are $\pi\text{--}\pi^*$ in nature [14]. Overall the electronic properties are typical for pyridyl and pyrazine triazole complexes by comparison with complexes **3** and **4** [15]. For the pyridine-1,2,4-triazole based complex, **1a**, the absorption spectra of the protonated and deprotonated species are very different, with a substantial blue shift in the λ_{max} occurring upon protonation (~ 40 nm) (see Fig. 2). However, for the pyrazine-1,2,4-triazole based complex, **2a**, only a small blue shift in the λ_{max} of the $^1\text{MLCT}$ absorption bands occurs upon protonation (~ 10 nm) (Fig. 2). Difference spectra (see supplementary information, Fig. S2) show the changes more clearly, with a blue-shift in the visible absorption bands upon protonation and a red-shift in the $\pi\pi^*_{\text{bpy}}$ transition in the UV region. The effect of protonation on the pyridine and pyrazine bound isomers are similar to those of related mononuclear complexes (see Table 1). In strongly acidic solution (conc. H_2SO_4), complex **1a** shows relatively minor changes in its absorption spectrum, whilst in contrast very dramatic changes in the absorption spectrum of **2a** are observed, with a blue-shift in the $^1\text{MLCT}$ absorption bands and the appearance of a very strong absorption at ~ 550 nm. For the mononuclear complexes a progressive modification of the absorption spectrum was observed ± 1 pH unit either

Table 1
Photophysical and redox properties (lifetimes for deuteriated complexes in parentheses)

	$\lambda_{\text{Abs}}/\text{nm}^{\text{a}}$	$E_{1/2}(\text{V vs SCE})^{\text{a}}$	$\lambda_{\text{lum}}/\text{nm}^{\text{a}}$	pK_{a}^{b}	$\tau_{298\text{ K}}/\text{ns}^{\text{a}}$	$\tau_{77\text{ K}}/\mu\text{s}^{\text{a}}$	Ref.
1a	245, 291, 480	0.86 (1.62 irr)	683	3.05	110 (135)	3.01 (4.00)	^c
H1a	242, 286, 439	1.19 (1.67 irr)	613	–	15 (6)	5.76 (7.62)	^c
1a ⁺	570, 1050 ^b	–	–	–	–	–	[2a]
2a	244, 289, 455	0.95 (1.55 irr)	664	2.15	82 (184)	7.85 (8.75)	^c
H2a	245, 284, 438	1.23 (1.55 irr)	672	–	312 (320)	7.34 (7.56)	^c
H2a	361, 543	–	–	–	–	–	^c
2a ⁺	570, 1060 ^b	–	–	–	–	–	[2a]
3	465	0.83	650	4.1	145 (183)	–	[15]
H3	437	1.14	620	–	–	–	[15]
4	445	1.01	668	3.7	230 (283)	4.45 (7.03)	[15]
H4	441	1.25	658	–	230 (230)	4.77 (6.00)	[15]

^a In CH_3CN .

^b In H_2O .

^c This work.

Fig. 2. Absorption Spectra for **1a** (left) and **2a** (right) in conc. H_2SO_4 (solid line), pH 1.5 (dotted line) and pH 7 (dashed line).

side of the pK_a point, with isosbestic points being maintained throughout the titration.

The acid dissociation constants (pK_a) for all complexes are given in Table 1. The values were obtained from the change in the absorption spectra of the complexes with changing pH (see Fig. S2). The behaviour observed can be rationalised by protonation/deprotonation of the triazole moiety. The acidity of the coordinated triazole ring has been found to be dependent on the nature of the non-coordinated substituent in the C3 position of the 1,2,4-triazole. This dependence is reflected in the change in pK_a , with respect to the unsubstituted C–H analogues **3** and **4**, Table 1 [16]. Protonation of the coordinated pyrazine ring, in **2a** and **4**, although possible, occurs at only at negative pH [2].

All complexes examined are luminescent in acetonitrile and, weakly, in aqueous solution, at room temperature and in EtOH/MeOH glass at 77 K. The complexes emit in the 600–700 nm region and a large blue shift is observed between 300 and 77 K, typical for $^3\text{MLCT}$ emission [13]. Emission lifetimes at 77 and 298 K measured at the emission maxima indicated are collected in Table 1. As for the absorption spectra, the emission maxima of **1a** and **2a** are close to those of the related complexes **3a** and **4a** respectively. Protonation of **1a** results in a blue shift in the emission and a reduction in emission lifetime, while for **2a**, protonation results in a modest red-shift in the emission spectrum with an increase in emission lifetime. The effect of deuteration of the bpy ligands on the emission lifetime of **1a** and **H1a** is not very significant at 298 K (Table 1). However at 77 K in alcoholic glass a more pronounced deuteration effect is observed for both the protonated and deprotonated species. In contrast, for **2a** a larger deuteration effect is observed at 298 K and (but less so at) 77 K (+12%). For the protonated pyrazine based complexes **H2a**, no deuteration effect is observed at either temperature. A notable feature for complex **4**, is the occurrence of a dual emission between 120 and 180 K [15]. A similar effect was observed (Fig. S4) for **2a**

suggesting that the excited state electronic structure in both complexes is similar.

3.1. Raman spectroscopy

Resonance Raman spectroscopy is widely employed in elucidating the ground and excited state properties of Ru(II) polypyridyl complexes, due to the selective enhancement of vibrational modes that are coupled to allowed spectroscopic transitions [17]. Such selective enhancement may assist in elucidating the nature of particular transitions, for instance the extent to which they are centred or localised on specific orbitals of individual ligands in the molecule. This level of detail in the assignment of the transitions leading to population of the lowest excited states is of particular importance in the development and study of photoactive and luminescent transition metal complexes [1].

Non-resonant Raman spectra of **1a/1b** and **2a** (powder samples) were recorded at 785 nm to provide a general overview of the (Raman-active) vibrational modes and are shown in Fig. 3. Deuteration enables direct assignment of bpy based vibrational bands (at 1600, 1484, 1317, 1269, 1171, 1057, 1033, 761 and 642 cm^{-1}) [18] and the pytrth $^-$ (at 1606, 1552, 1514, 1462, 1435, 1388, 1344, 1299, 1184, 1147, 1100, 1014, 949, 761, 646 cm^{-1}) and pztrth $^-$ (1552, 1460, 1418, 1356, 1168, 1143, 1102, 945, 651 cm^{-1}) based vibrational bands.

Resonance Raman (rR) spectra were recorded for **1a/b**, **H1a/b**, **2a/b** and **H2a/b** in aqueous solution at 457.9 and 488 nm and at 514.5 nm for **H2a/b**. For **1a/1b** and **H1a/H1b** only [H₈]-bpy and [D₈]-bpy based vibrational features respectively were observed at 457.9 and 488 nm (see Figs. S5 and S6, supplementary information), confirming the $^1\text{MLCT}_{\text{bpy}}$ character of the lowest absorption bands and the absence of transitions associated with the pytrth $^-$ and Hpytrth ligands. In contrast, for **2a/b**, **H2a/b**, although vibrational features associated with [H₈]-bpy and [D₈]-bpy are observed, additional bands associated with pztrth $^-$ and Hpztrth are observed also (Figs. 4 and 5). For **2a/b**, additional

Fig. 3. (Solid state) Raman spectra of **2a** (upper), **1a** (middle) and **1b** (lower) at 785 nm.

vibrational bands at 1602, 1516, 1373 and 1194 cm^{-1} are observed at both 457.9 and 488 nm excitation.

For **H2a/b**, in addition to bpy features, bands assigned to the Hp2trth ligand are present at 1587, 1549, 1513, 1440, 1387, 1293, 1206, 1187 and 1073 cm^{-1} . For **H22a/b** no vibrational features assignable to $[\text{H}_8]\text{-bpy}/[\text{D}_8]\text{-bpy}$ are observed at either 457.9 or 488 nm. Bands at 1634, 1544, 1494 and 1472 cm^{-1} are insensitive to deuteration and are assigned to the doubly protonated $\text{H}_2\text{p2trth}$ ligand.

Resonance Raman spectra of the oxidised complexes **1a**⁺ and **2a**⁺, in H_2O , (Fig. 6) in contrast to those of **1a/2a**, show no characteristic $[\text{H}_8]\text{-bpy}$ features. The excitation wavelength used is resonant with a strong absorption assigned as a ligand to metal charge transfer (LMCT) band. The absence of vibrational bands assignable to bpy ligand vibrations is not unexpected since the oscillator strength of LMCT absorptions has been shown to be dependent on the electron donor properties of the ligands [19]. In the present case the electron rich triazole-thiophene ligand results in a much more intense LMCT absorption band than expected for this class of complex and hence the observation of vibrational bands not assignable to the bpy

ligand supports the assignment of the absorption to a $\text{py}(\text{z})\text{trth}$ -to-metal charge transfer band.

3.2. Transient resonance Raman spectroscopy

Transient resonance Raman spectra of **1a** and **2a** in CD_3CN , both in a deprotonated and protonated state, are shown in Fig. 7. The observation of strong bands at 1212 and 1285 cm^{-1} in the spectra of **1a/H1a** and **2a**, readily attributable to the bpy anion radical, confirm the assignment of the lowest emissive state as being from a bpy-based $^3\text{MLCT}$. In the case of **H2a**, there is a notable absence of these bands. On the basis of transient absorption spectra of the related complexes **3** and **4**, the absence of excited state resonance in the spectrum of **H2a**, due to a shift in the excited state absorption out of resonance with the 355 nm excitation line may be discounted. Based on earlier transient Raman studies of **4** [15], it can be concluded that for **H2a** the lowest excited state is pyrazine-based. In aqueous solution, a similar situation is observed.

In the spectra of **1a** and **2a** bands assigned to the 1,2,4-triazole based ligands are also observed, suggesting

Fig. 4. Resonance Raman Spectra of (i) **2a** (ii) **2b** (iii) **H2a** (iv) **H2b** (v) **H₂2a** at 457.9 nm excitation.

Fig. 5. resonance Raman spectra of (i) **1a** (ii) **2a** and (iii) **H2a** 488 nm excitation.

Fig. 6. Resonance Raman spectra of (a) **1a**⁺ and (b) **2a**⁺, in basic/H₂O at 785 nm.

contributions from pyrth- and pztrth-based absorptions at 355 nm [20].

3.3. Density functional theory

In order to gain more insight into the electronic properties of the complexes **2a/H2a** and **2b/H2b**, DFT

calculations were carried using the B3LYP functional and the LanL2DZ basis set. For the protonated complex a complication arises in regard to the point of protonation, whether it is at N1 or N4 (Fig. 1). Previous studies on the relative reactivity of the uncoordinated nitrogen ligands of the 1,2,4-triazole ring have indicated that the N1 position is slightly less acidic than the N4 position. However, due to

Fig. 7. Transient Raman spectra of (a) **H2a**, (b) **2a**, (c) **H1a** and (d) **1a** in CD₃CN (λ_{exc} 355 nm).

the potential of introducing additional steric interactions in protonation at the N1 position, in the present study, the N4 position of the 1,2,4-triazole was protonated for the DFT calculations of **H2a/b**.

After geometry optimization with an ultrafine integration grid, the molecular orbitals were described in terms of contributions from various groups in the molecule for **2a** and **H2a**: *Ru*—the Ru atom, *pz*—the pyrazine ring, *tr*—the triazole moiety; *th*—the thiophene moiety; *bpy1*

and *bpy2*—the two bipyridines. These data are shown in Fig. S7 of the supplementary information. The isosurfaces for the HOMO-1, HOMO, LUMO and LUMO+1 of **2a** and **H2a** are shown in Fig. 8. In the frontier region, neighboring orbitals are often closely spaced. In such cases, consideration of only the HOMO and LUMO may not yield a realistic description of the frontier orbitals. For this reason, partial density of states (PDOS) diagrams, which incorporate a degree of overlap between the curves

Fig. 8. Isosurfaces of HOMO-1, HOMO, LUMO and LUMO+1 orbitals for **2a** (left) and **H2a** (right).

Fig. 9. PDOS diagrams for **2a** (top) and **H2a** (bottom).

convoluted from neighboring energy levels, can give a more representative picture of the nature of the frontier orbitals. The PDOS diagrams obtained are shown in Fig. 9.

DFT calculations were used to predict the Raman spectrum of **2a/H2a** and **2b/H2b** (Table 2). A systematic error occurs in the calculation of vibrational frequencies due to the consistent underestimation of bond length, for example, and the neglect of anharmonicity. To compensate a scaling factor is used. The ‘Solver’ module of Microsoft Excel™ was used to achieve the best fit of the experimental peaks with those obtained from the calculations. The spectra of the perprotio and deuterio complexes were compared, with the bands which were sensitive to bpy deuteration being assigned as bpy-based. The isotope shift observed

upon deuteration in the calculated spectra is demonstrated in Fig. 10.

4. Discussion

The UV–Vis absorption and emission properties of the mononuclear complexes show a close comparison with those of the analogous complexes **3** and **4**, but are slightly red shifted. Upon protonation for both complexes a blue shift in the absorption spectra is observed. For **1a** protonation results in large blue shift (~ 70 nm), in agreement with observations on other mononuclear pyridyl-1,2,4-triazole complexes. For **2**, protonation results, first in a very minor red shift,

Fig. 10. Calculated Raman Spectra for **H2a** (upper trace) and **H2b** (lower trace).

followed by a blue shift in the emission λ_{max} , with a concomitant reduction in intensity. Again the acid-base emission properties bear close comparison with related systems. The $\text{p}K_{\text{a}}$ values determined for both complexes are lower than for **3** and **4**. This confirms the electron withdrawing nature of the thienyl group. As is typical, the pyrazine complex is more acidic than the analogous pyridine complex, due to the greater electron withdrawing nature of the pyrazine ring [16].

The results obtained in the present study provide a basis for a more detailed understanding of the nature of the interaction between the thienyl and ruthenium(II) -based components of these simple dyads. Although it is tempting to consider the thienyl group as an innocent part of the Hpytrth and Hpztrth ligands, in electronic terms such a simplification is not appropriate for understanding the overall properties of the systems. Our intention in this study was to build on the extensive body of data available on 1,2,4-triazole based systems, to explore in a fundamental way the extent to which different moieties in relatively simple dyads can be viewed as distinct groups. It is clear from examination of the properties of the complexes in their ground and their electronic states that the degree of interaction between the components is critically dependent on the electronic state (i.e. ground or excited) and that extrapolating conclusions based on study of ground state interaction to excited state systems is not always justified. In the present contribution, extensive resonance Raman spectroscopic investigations of both the ground and lowest excited electronic states together with computational analysis (DFT) are employed to help understand the excited state electronic structure of these systems.

For the complex containing the pyridyl-triazole moiety only the bpy ligands are involved in the absorption process, in both of the protonation states. Pyrazine is a better π -acceptor than pyridine. For **2**, therefore, the π^* level is reduced, leading to an overlap in the triazole and bpy absorption bands. Protonation of the triazole leads to

a reduction of the electron density on the metal centre. This is reflected in an increase in the oxidation potential, however it does not change the overlap of bpy and Hthpztr in the $^1\text{MLCT}$ state. Transient Resonance Raman studies agree with the results from both the DFT and excited state lifetime measurements. Bpy anion radical peaks observed in **2** indicate that the excited state is localised on the bpy moiety while in the protonated complex no bpy radical peaks are observed.

For **2a**, the HOMO is based on thiophene and triazole (Fig. 8). The LUMO is on one of the bpy ligands. The same information is shown in the PDOS spectrum in Fig. 9. In addition, the PDOS spectrum for **2a** shows that the π^* orbital of the pyrazine ligand is at higher energy than that of the bpy (Fig. 9). The metal-based frontier orbitals are the HOMO-2 to HOMO-4 (Fig. S7).

In contrast, the HOMO of **H2a** has an increased contribution from the Ru center (Fig. 8). The location of the LUMO has changed from bpy to pyrazine. The PDOS spectrum shows the overall changes in electronic structure. In the protonated complex, the metal center has a large contribution to the first four occupied orbitals (Fig. S7). The PDOS spectrum of **H2a** is shifted to lower energy by about 3.5 eV, compared to that of **2a**. This indicates the increased difficulty in removing an electron from the HOMO of **H2a**, which is due to the increased charge on the complex. A comparison of the PDOS spectra of **2a** and **H2a** shows that the π^* orbital of the pyrazine is shifted to lower energy on protonation, so that the LUMO is now pyrazine-based.

The main point to emphasise is the contrast in the degree of interaction between the metal center and the thienyl moiety in the ground and excited states. In the ground state, **2a** shows contributions from both the thienyl and the Ru in the levels H-4 to HOMO, which may be considered the occupied frontier orbitals. However in the excited state the unoccupied frontier orbitals, LUMO to LUMO+4, show increased contributions from the bpy moieties but little or no contributions from the Ru and thienyl. A similar picture emerges for **H2a**. This suggests appreciable delocalisation of the HOMO and is also consistent with the proposal [2] that the significant interaction in the mixed valence thienyl bridged dimers **5** and **6** is indeed due to HOMO assisted superexchange.

The absence of any contribution from the pyrazine ring for **2a** and **H2a** is in agreement with the similarity of the spectra for **1a**⁺ and **2a**⁺ at 514 nm (LMCT bands).

The calculated isosurfaces for the LUMO and LUMO+1 have been used to approximate the location of the $^3\text{MLCT}$ excited state in **2a** and **H2a**. There are a number of assumptions which must be borne in mind, namely: that the virtual Kohn-Sham orbitals from the DFT calculations are equivalent to unoccupied orbitals; that the lowest energy transition is to the lowest unoccupied orbitals; and that the $^1\text{MLCT}$ is located on the same ligands as the $^3\text{MLCT}$ state. In previous studies deuteration has been used to investigate the location of the excited state [21]. If the excited state is

Table 2
Calculated and experimental Raman frequencies for bpy and triazole vibrations in **H2a**

Experimental bpy (cm ⁻¹)	Calculated bpy (cm ⁻¹)	Experimental Hthpztr (cm ⁻¹)	Calculated Hthpztr (cm ⁻¹)
1608	1606	1517	1526
1561	1563	1440	1449
1492	1492	1394	1408
1320	1328	1210	1215
1175	1187	1194	1208

A scaling factor of 0.978 was used.

located on the ligand, which has been deuterated then the excited state lifetime is seen to increase. In **2a**, deuteration of the bpy ligands leads to an increase in lifetime from 82 to 184 ns (Table 1), indicating that the excited state is bpy-based. This is consistent with the location of the LUMO and LUMO+1 electron density suggested by the calculations. For **H2a**, computational studies predict that the excited state will be based on the pyrazine-triazole ligand. As would be expected, deuteration of the bpy ligands in this complex has no effect on the excited state lifetime in this case (Table 1).

5. Conclusions

Resonance Raman spectroscopic investigations of the complexes in both the ground and lowest excited electronic states, coupled with photophysical measurements as a function of pH, have been employed to help understand the excited state electronic structure of these simple thienyl dyad systems. The influence of deuteration on the emission lifetimes provided further evidence as to the nature of the lowest emissive excited state/s involved. DFT calculations have been used to supplement the experimental data, representing the first example of DFT work on Ru(II) monomer complexes containing the 1,2,4-triazole moiety. The overall pattern of results, which emerge from this joint theoretical/experimental approach underlines the fact that the degree of interaction between the components depends very much on the electronic state, i.e. ground or excited, under consideration. The results suggest that the extrapolation of conclusions based solely on the study of ground state interaction between molecular components to the interaction in the corresponding excited state is not necessarily justifiable.

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Appendix. Supplementary Material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2004.10.114

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