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Proton Controlled Intramolecular Communication in Dinuclear Ruthenium(II) Polypyridine Complexes

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The synthesis and characterization of two dinuclear ruthenium polypyridyl complexes based on the bridging ligands 5,5′-bis(pyridin-2-′-yl)-3,3′-bis(1H-1,2,4-triazole) and 5,5′-bis(pyrazin-2-′-yl)-3,3′-bis(1H-1,2,4-triazole) and of their mononuclear precursors are reported. The dinuclear compounds have been prepared by a Ni(0) catalyzed coupling of a mononuclear ruthenium(II) polypyridyl complex containing a brominated triazole moiety. Electrochemical and photophysical studies indicate that, in these dinuclear complexes, the protonation state of the bridge may be used to tune the intercomponent interaction between the two metal centers and that these species act as proton driven three-way molecular switches that can be read by electrochemical or luminescence techniques.

Introduction

Ruthenium(II) polypyridine complexes are playing a key role for the development of multicomponent (supramolecular) systems capable of performing photo- and/or redox-triggered functions. Examples are artificial antenna systems,¹ charge separation devices for photochemical solar energy conversion,¹ and information storage devices.² Of particular interest in this regard are molecular components with well-defined photophysical and redox properties, which can be switched in this regard are molecular components with well-defined photophysical and redox properties, which can be switched or tuned by external perturbation.³

For the past number of years, there has been considerable interest in the study of mononuclear and multinuclear ruthenium(II) polypyridyl complexes containing ligands such as 3,5-bis(pyridin-2-′-yl)-1H-1,2,4-triazole (Hbpzt)⁴ and 3,5-bis(pyrazin-2-′-yl)-1H-1,2,4-triazole (Hbzpt)⁵ (Figure 1). It has been shown that for dinuclear compounds featuring these ligands strong interaction is observed between metal centers.⁶

In this contribution, the syntheses and spectroscopic, photophysical, and redox properties of two new dinuclear ruthenium(II) complexes [(bpy)₂Ru(bpzbt)Ru(bpy)₂]₂⁺ (1) (where H₂bpzt is 5,5′-bis(pyridin-2-′-yl)-3,3′-bis(1H-1,2,4-triazole) and [(bpy)₂Ru(bpzbt)Ru(bpy)₂]₂⁻ (2) (where H₂-bpzt)}


bpbt = 5,5′-bis(pyrazin-2-yl)-3,3′-bis(1H-1,2,4-triazole)) are reported, together with the synthesis and characterization of their mononuclear precursors. The structures of 1 and 2, of the dinuclear compounds [(Ru(bpyp)2)(bpt)]3+ (3) and [(Ru(bpyp)2)(bpzt)]3+ (4), and of some other mononuclear analogues, used for comparison, are shown in Figure 1.

A first feature of this study is the manner in which the title compounds have been synthesized. The N2 and N4 coordination sites of the triazole ring are nonequivalent, and direct synthesis of the dinuclear species from the bridging coordination sites of the triazole ring are nonequivalent,7 and possible isomers are shown in Figure 2. The dinuclear compounds have been prepared by a Ni(0) catalyzed homonuclear coupling of a bromine substituted ruthenium(II) polypyridyl complex. With this synthetic method, a single well-defined product is obtained.

The second purpose is the investigation of the intercomponent processes in 1 and 2 as a function of the protonation state of the bridging ligand. The important observation is that by control of the protonation of the bridge component processes in 1 a three-way proton controlled molecular switch is obtained, or better. A first feature of this study is the manner in which the observation is that by control of the protonation of the bridge product is obtained. With this synthetic method, a single well-defined product is obtained.

The second purpose is the investigation of the intercomponent processes in 1 and 2 as a function of the protonation state of the bridging ligand. The important observation is that by control of the protonation of the bridge component processes in 1 a three-way proton controlled molecular switch is obtained, or better. A first feature of this study is the manner in which the observation is that by control of the protonation of the bridge product is obtained. With this synthetic method, a single well-defined product is obtained.

**Experimental Section**

**Materials.** All solvents used for spectroscopic measurements were of Uvasol (Merck) grade. All other reagents were HPLC grade or better. cis-[Ru(bpy)2Cl2]2H2O was prepared by standard procedures. Complexes 3–6 have been prepared by previously reported procedures.4–7

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**Figure 1.** Complex structures.

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**Figure 2.** Possible coordination isomers formed by direct reaction of H2-bpbt or H2-bpzt with cis-[Ru(bpyp)2Cl2].

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**Synthetic Methods.** 3-Bromo-5-(pyridin-2-yl)-1H-1,2,4-triazole (HBrpytr). A suspension of 3-(pyridin-2-yl)-1H-1,2,4-triazole (880 mg, 6 mmol) in H2O (15 mL) was dissolved by slow addition of 10 M NaOH (pH ~ 12). Subsequently, 0.6 mL of Br2 (99%: d = 3.199 g/mL) was added slowly while maintaining a pH of 12 by addition of concentrated NaOH solution. After stirring for 3 h, the solution was acidified to pH 3–4 with 5 M HCl (aq), resulting in precipitation of the brominated ligand, which was collected by suction filtration. Yield: 945 mg (70%). 1H NMR data d6-DMSO: H3, 8.60 ppm (d); H4, 7.85 ppm (t); H5, 7.49 ppm (t); H6, 8.00 ppm (d).

3-Bromo-5-(pyrazin-2-yl)-1H-1,2,4-triazole (HBrpztr). This compound was obtained from 3-(pyridin-2-yl)-1H-1,2,4-triazole using the method described for HBrpytr. Yield: 920 mg (65%). 1H NMR data d6-chloroform: H3, 9.40 ppm (s); H5, 8.72 ppm (d); H6, 8.65 ppm (d).

cis-[Ru(bpyp)2Brpy]PF6·H2O. A suspension of HBrpytr (200 mg, 0.9 mmol) and cis-[Ru(bpyp)2Cl2]·2H2O (348 mg, 0.67 mmol) in 20 mL of EtOH/H2O (1:1, v/v) was heated at reflux for 2 h. After cooling to room temperature, the reaction mixture was filtered and reduced in volume in vacuo. Two drops of a 30% NH4OH solution were added prior to addition of saturated aqueous solution of NH4PF6 (3 mL) to induce precipitation. The solid was separated by vacuum filtration and washed with 20 mL of diethyl ether. The red-orange product was obtained in a pure form by recrystallization from acetone/water (1:1, v/v). Yield: 59%. 1H NMR data d6-acetonitrile: 7.15 ppm (dd, 1H), 7.30 ppm (dd, 1H), 7.42 ppm (dd, 1H), 7.51 ppm (dd, 1H), 7.59 ppm (dd, 1H), 7.70 ppm (dd, 1H), 7.83 ppm (dd, 1H), 7.90 ppm (dd, 1H), 7.99 ppm (m, 3H), 8.03 ppm (dd, 1H), 8.52 ppm (dd, 1H), 8.56 ppm (dd, 1H), 8.66 ppm (dd, 2H). UV–vis absorption spectroscopy: λmax = 290 nm (ε = 11600 M−1 cm−1). Luminescence spectroscopy: λmax = 665 nm, τ = 250 ns at 295 K in deaerated acetonitrile. Acid/base properties: pK1, 1.3, pH 0.9. Anal. Calcld for C27H20N8PRu: C, 40.50%; H, 2.75%; N, 14.06%. Found: C, 40.79%; H, 2.57%; N, 13.94%. Mass spectroscopy: molecular ion (for C27H20N8PRu...
RuBr=) at 637/639 m/z units (19Br/81Br). The isotopic pattern is in agreement with theoretical values.

[Ru(bpy)3(Brptz)][PF6·H2O; cix·[Ru(bpy)2Cl2]·2H2O (519 mg, 0.67 mmol)] with 300 mg (0.9 mmol) of HBr was heated at reflux in 20 mL of EtOH/H2O (1:1, v/v) for 3 h. The pure complex was obtained using the method described for [Ru(bpy)3(Brpy)]+−PF6·H2O. Yield: 64%. 1H NMR δacetonicitrile: 7.35 ppm (dd, 1H), 7.41 ppm (dd, 1H), 7.45 ppm (dd, 1H), 7.53 ppm (dd, 1H), 7.71 ppm (dd, 1H), 7.76 ppm (dd, 1H), 7.83 ppm (dd, 1H), 7.9 ppm (m, 3H), 8.06 ppm (m, 3H), 8.22 ppm (d, 1H), 8.58 ppm (dd, 2H), 8.65 ppm (dd, 2H), 9.02 ppm (d, 1H). UV−vis absorption spectroscopy: λmax = 450 nm (ε = 12900 M−1 cm−1). Luminescence spectroscopy: λmax = 647 nm, τ = 200 ns at 298 K in deaerated acetonitrile. Acid/base properties: pKa, 1.4, pH, 1.5/5. Precal. Calcld. for C25H16BrN4P2Ru: C, 39.00%; H, 2.62%; N, 15.73%. Found: C, 39.47%; H, 2.69%; N, 15.24%. Mass spectroscopy: molecular+ ion (C25H18BrN4RuBr+) at 638/640 m/z units (19Br/81Br). The isotopic pattern is in agreement with theoretical values.

The second red-orange band was collected, and the solvent was evaporated under reduced pressure.

The deep-red product obtained was recovered by filtration and was purified by recrystallization from acetonewater (1:1, v/v) with 2 drops of 30% NH4OH and 3 mL of a saturated aqueous solution of NH4PF6. The product was separated by filtration, dissolved in a small volume of MeCN/MeOH (50:1, v/v), and purified by chromatography on neutral alumina with MeCN/MeOH (50:1, v/v). The second red-orange band was collected, and the solvent was evaporated under reduced pressure.

Elemental analysis has been carried out at the Microanalytical Laboratory at University College Dublin.

Electrochemical measurements were carried out on a Model 660 electrochemical workstation (CH Instruments). Typical complex concentrations were 0.5−1 mM in anhydrous acetonitrile containing 0.1 M tetraethylammonium perchlorate (TEAP). A Teflon shrouded glassy carbon working electrode, a Pt wire auxiliary electrode, and an SCE reference electrode were employed. Solutions for reduction measurements were deaerated by purging with N2 or Ar gas for 15 min prior to the measurement. Measurements were made in the range −2.0 to 2.0 V versus SCE. Protonation of complexes was achieved by addition of 0.1 M trifluoromethanesulfonic acid in acetonitrile. pH cyclic voltammograms were obtained at sweep rates of 20, 50, 200, and 500 mV s−1; differential pulse voltammetry (DPV) experiments were performed with a scan rate of 20 mV s−1, 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 composed 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, which was a pseudo-Ag/AgCl reference electrode. The working electrode was held at the

The H NMR spectral data shown in Figure 4 illustrate the been fully characterized using spectroscopic measurements.

Symmetric nature of the complexes. Spectral assignments are given in the Experimental Section.

**Photochemical Properties.** All spectroscopic data for complexes 1 and 2 are presented in Table 1, together with data for model complexes 3–6. The absorption spectra of complexes 1 and 2 show intense bands in the UV region \( \lambda_{\text{max}} = 243 \text{ nm (} \varepsilon = 52500 \text{ M}^{-1} \text{ cm}^{-1}) \), 290 nm \( \varepsilon = 124100 \text{ M}^{-1} \text{ cm}^{-1}) \); 2, 244 nm \( \varepsilon = 53400 \text{ M}^{-1} \text{ cm}^{-1}) \), 288 nm \( \varepsilon = 126600 \text{ M}^{-1} \text{ cm}^{-1}) \) and moderately intense bands in the visible region \([1, 480 \text{ nm (} \varepsilon = 17400 \text{ M}^{-1} \text{ cm}^{-1}) ; 2, 455 \text{ nm (} \varepsilon = 25400 \text{ M}^{-1} \text{ cm}^{-1}) \) are typical for these types of complexes.\(^5\) The complexes are luminescent in acetonitrile at 298 K, and excitation spectra match closely the absorption spectra. Luminescence lifetimes at room temperature are strictly single exponential and are in the 100–1000 ns time domain. Luminescence quantum yields at room temperature are of the order of 10^(-3) (Table 1).

**Acid–Base Properties.** The spectroscopic, photophysical, and redox properties (vide infra) of 1 and 2 are dependent on the protonation state of the complex. For 1, in aqueous buffered solution, UV–vis spectroscopy as a function of pH yields two reversible protonation steps with pK\(_a\) values of 1.1 and 3.8. On the basis of former protonation studies on Ru(II) complexes containing triazole ligands,\(^12\) the protonation processes can be attributed to protonation of the triazole rings. However, the two successive pK\(_a\) values obtained suggest that the triazole rings interact and the monoprotonated species is better viewed as a compound where the added proton is shared between the two triazole units of the bridging ligand. As with the structurally similar mononuclear complexes 5 and 6, protonation results in a blue shift in the UV–vis absorption spectra. Complex 2, as observed for 6, shows only minor changes in its UV–vis spectra upon protonation, and hence, reliable determination of pK\(_a\) values is not possible. For 2, additional protonation states exist via protonation of pyrazine; however, such protonation occurs only at very negative pH and need not be considered in the pH range studied.\(^7\)

The emission properties of 1 and 2 also show pH dependence (see Table 1). Emission spectra obtained for 1

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**Table 1.** Electronic, Photophysical, and Redox Data for Complexes 1–6

<table>
<thead>
<tr>
<th></th>
<th>absorption ( \lambda_{\text{max}} ) ( \text{nm} )</th>
<th>emission, 298 K ( \lambda_{\text{max}} ) ( \text{nm} ), ( (\tau, \text{ns}) ) ( \Phi \times 10^{-1} )</th>
<th>( E (\text{ox}) ) V vs SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>([\text{bpy}]_2\text{Ru(bppb)}\text{(Ru(bpy)}_2\text{)}] ( ^{2+} )</td>
<td>480</td>
<td>690 (102) ( (2.4) )</td>
</tr>
<tr>
<td>H1</td>
<td>([\text{bpy}]_2\text{Ru(bppb)}\text{(Ru(bpy)}_2\text{)}] ( ^{3+} )</td>
<td>440</td>
<td>660 (344) ( (2.1) )</td>
</tr>
<tr>
<td>H2</td>
<td>([\text{bpy}]_2\text{Ru(Hbpzt)}\text{(Ru(bpy)}_2\text{)}] ( ^{3+} )</td>
<td>431</td>
<td>630 ( (&lt;5 \text{ ns}) )</td>
</tr>
<tr>
<td>3</td>
<td>([\text{bpy}]_2\text{Ru(bpp)}\text{(Ru(bpy)}_2\text{)}] ( ^{2+} )</td>
<td>452</td>
<td>648 (80)</td>
</tr>
<tr>
<td>5</td>
<td>([\text{bpy}]_2\text{Ru(pytr)}] ( ^{3+} )</td>
<td>467</td>
<td>650 (145)</td>
</tr>
<tr>
<td>H5</td>
<td>([\text{bpy}]_2\text{Ru(Hpytr)}] ( ^{3+} )</td>
<td>438</td>
<td>612 ( (&lt;1 \text{ ns}) )</td>
</tr>
<tr>
<td>2</td>
<td>([\text{bpy}]_2\text{Ru(bpzbt)}\text{(Ru(bpy)}_2\text{)}] ( ^{2+} )</td>
<td>455</td>
<td>670 (214) ( (3.4) )</td>
</tr>
<tr>
<td>H2</td>
<td>([\text{bpy}]_2\text{Ru(bppb)}\text{(Ru(bpy)}_2\text{)}] ( ^{3+} )</td>
<td>436</td>
<td>675 (764)</td>
</tr>
<tr>
<td>H1</td>
<td>([\text{bpy}]_2\text{Ru(Hbpzt)}\text{(Ru(bpy)}_2\text{)}] ( ^{3+} )</td>
<td>430</td>
<td>678 (1000) ( (7.2) )</td>
</tr>
<tr>
<td>H4</td>
<td>([\text{bpy}]_2\text{Ru(bpp)}\text{(Ru(bpy)}_2\text{)}] ( ^{2+} )</td>
<td>440</td>
<td>690 (106)</td>
</tr>
<tr>
<td>6</td>
<td>([\text{bpy}]_2\text{Ru(pytr)}] ( ^{2+} )</td>
<td>458</td>
<td>660 (250)</td>
</tr>
<tr>
<td>H6</td>
<td>([\text{bpy}]_2\text{Ru(Hpytr)}] ( ^{3+} )</td>
<td>441</td>
<td>665 (430)</td>
</tr>
<tr>
<td>2</td>
<td>([\text{bpy}]_2\text{Ru(bpzbt)}\text{(Ru(bpy)}_2\text{)}] ( ^{2+} )</td>
<td>452</td>
<td>620 (1000)</td>
</tr>
</tbody>
</table>

\(^{a}\) Bracketed numbers ([ ] ) refer to the number of electrons under the wave. \(^{b}\) In acetonitrile at 298 K. Data for the mononuclear pyridine and pyrazine model compounds \([\text{Ru(bpy)}_2\text{(pytr)}]^{2+} \) and \([\text{Ru(bpy)}_2\text{(pztr)}]^2\) are included for comparison.
Dinuclear Ru(II) Polypyridine Complexes

The emission spectrum of 1, H1, and H2-1 in acetonitrile (protonation with CF3SO3H acid).

Figure 5.

At three different protonation states are shown in Figure 5. The emission spectrum of 1 undergoes a blue shift from 690 nm (1) to 660 nm (H1) to 630 nm (H2-1) in acetonitrile. The inflection points of the emission titration curves (pH) are observed at pH 0.45 and 2.7 in buffered aqueous solution (see Experimental Section). Single protonation of 1 to H1 results in an increase of emission lifetime, in contrast with the effect of the protonation of the mononuclear complex 5. However, the doubly protonated complex H2-1 compares well in terms of emission energy and emission lifetime with H5.

For 2, protonation results in a small red shift in the emission spectrum (~10 nm) in agreement with similar pyrazine based complexes (e.g., 6/H6).13 Compared with 1, the changes in emission energy are much smaller, but the emission lifetime of the emitting state increases with each protonation step. It should be noted that protonation of the pyrazine ring in the exited state is easier than in the ground state. For H6/H2-6, a pH value of 2.0 has been reported. Because this process leads to quenching of the emission, the acidity of the measuring solution needs to be controlled carefully.

Redox Properties. The metal based oxidation potentials for 1 and 2 and for their protonated forms together with those of the model compounds are collected in Table 1. Both 1 and 2 undergo several reversible oxidation and reduction processes within the redox window investigated (between +2.0 and −2.0 V vs SCE) (see Figure 6). For both 1 and 2, the first metal oxidation potential is close to that of monomers 5 and 6, respectively, and at lower potential than those of dinuclear complexes 3 and 4. For both 1 and 2, an increase in the metal based oxidation potentials is observed upon protonation, together with a significant decrease in the gap between the first and second oxidation waves, from ~135 mV for both 1 and 2 to less than 70 mV for H1 and H2. Both H2-1 and H2-2 exhibit a single two electron metal oxidation wave at potentials comparable to those observed for H5 and H6. The ligand based reduction processes are as expected for ruthenium polypyridyl complexes and are not further discussed.4,5

Spectroelectrochemistry. The visible–near-infrared spectra of 2, of the electrochemically generated mixed valence and fully oxidized species, are shown in Figure 7. Only minor differences are observed in the energy of the intervalence (IT) and ligand-to-metal-charge-transfer (LMCT) bands in 1 and 2 and in H1 and H2. For 1 and 2, the formation of the mixed valence species is identified by a decrease in the intensity of the MLCT bands at ~22220 cm−1 (450 nm) and the formation of new bands at ~5500 cm−1 and at 11000 and 17500 cm−1. Bulk electrolysis at a potential above the second oxidation wave results in the complete depletion of the 22220 cm−1 band coupled with a concomitant depletion of the band at 5500 cm−1 and a further increase in both bands at 11000 and 17500 cm−1. All processes are fully reversible.

Reversible spectroelectrochemistry is also observed for H1 and H2. For both compounds, after applying a potential of 1.2 V (vs pseudo-Ag/AgCl), the formation of a band at about 8700 cm−1 is observed; further increase of the potential past the second oxidation potential of the complex results in the formation of spectral features at 17860 and 11175 cm−1 with concomitant depletion of the band at 8700 cm−1. However, analysis of the IT bands is difficult, because they are located in an area of the spectrum where both LMCT and IT bands are expected. For the fully protonated complexes H2-1 and H2-2, no evidence for intervalence bands was found. However, in the presence of triflic acid, the fully oxidized H2-1 and H2-2 exhibit spectral features, most likely LMCT bands at 23360 and 12550 cm−1 that are, however, less intense and blue-shifted with respect to those of the mono- and deprotonated species.

Discussion

Synthesis and Characterization. As pointed out in the Introduction, the preparation of complexes with ligands such

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as $H_2$bpbt and $H_2$bpzbt is by no means straightforward. Because the N2 and N4 nitrogen atoms of the triazole ring are chemically nonequivalent, direct synthesis of the complexes from these ligands can yield five possible coordination isomers, on the basis of the binding mode of the five-membered ring (Figure 2). In three of these isomers (isomers a–c in Figure 2), the Ru(bpy)$_2$ moiety is bound to a pyridine (or pyrazine) and a triazole ring; in the other two isomers, coordination takes place via the two central triazole rings and does not involve the pyridine and pyrazine rings (isomers d and e in Figure 2). To avoid the formation of so many different coordination isomers, a new synthetic method was developed. This method is based on the Ni(0) catalyzed coupling reported for bromide containing organic compounds.

In this synthetic approach, brominated pyridine and pyrazine triazole ligands were prepared by adapting procedures previously reported for the bromination of 1,2,4-triazoles. These brominated ligands were subsequently complexed with cis-[Ru(bpy)$_2$Cl$_2$]$\cdot$2H$_2$O, and the products obtained from this complexation reaction were reacted with Ni(0) to produce the dinuclear complexes. With this method, the formation of complexes where the metal centers are coordinated to the two central triazole rings is prevented.

As already noted, the N2 and N4 coordination sites of the triazole ring (see Figure 2) are not equivalent, and therefore, the formation of coordination isomers is expected. The introduction of the bromine atom, although primarily for use in the coupling reaction, has the secondary effect that the presence of this bulky atom in the 3-position results in the formation of the N2 isomer (>95%) over the N4 isomer (<5%), with the N4 isomer being lost during subsequent recrystallization. Therefore, as a result of the synthetic strategy employed, 1 and 2 have been obtained as well-defined symmetrical dinuclear compounds where both metal centers are coordinated to a pyridine (1) or pyrazine (2) ring and N2 of the triazole moiety (isomer a in Figure 2). This is confirmed by the relative simplicity of the $^1$H NMR spectra. The spectra are very similar to those obtained for the N2 isomers of mononuclear model complexes 5 and 6. This similarity confirms that N2 coordination is retained in the coupling reaction, and the symmetry of the spectrum furthermore confirms that both metal centers are equivalent. This observation is not unexpected. Earlier studies have shown that the pyridyl- and pyrazyltriazoles are extremely stable under normal synthetic conditions and that isomerization is only observed for protonated complexes. Deprotonated complexes were found to be photostable.

Both 1 and 2 exhibit absorption and emission properties, which are characteristic for triazole based ruthenium poly-

evidence for communication between the two metal centers. They also indicate that this interaction is strongly dependent on the protonation state of the bridging ligand. The presence of two protonation steps with different $pK_a$ values provides further confirmation of this. The effect of communication on the emission behavior is most clearly demonstrated for H1 (Figure 5) and H2. In the absence of any interaction, two emission signals are expected for a monoprotonated species. For H1, where the emission energy values expected for the deprotonated (690 nm) and protonated species (630 nm) are significantly different, this would be particularly straightforward to detect. Instead, a single-exponential decay of the emission state is observed, and the emission at 660 nm is intermediate between that of 1 and H2H2. This indicates the presence of a new emitting species, in which the effect of monoprotonation is shared by both metal centers.

Electrochemical and spectroelectrochemical studies can be used to quantify this interaction. The first parameter of interest is the separation between the two metal-based oxidation processes ($\Delta E$). This separation is related to the stability of the intervalence compound Ru(II)Ru(III) as defined in eq 118

$$K_c = \exp(\Delta E/25.69)$$

where $K_c$ is the comproportionation constant as defined in eq 2

$$K_c = \frac{[\text{Ru}^2\text{Ru}^2][\text{Ru}^3\text{Ru}^3]}{[\text{Ru}^2\text{Ru}^3]^2}$$

The $\Delta E$ values obtained for the deprotonated compounds of 180 mV for 1 and 170 mV for 2 are indicative of a significant intramolecular communication (Table 2). This interaction is, however, less than that observed for 3 and 4, for which values of about 300 mV were obtained. For H1 and H2, the difference between first and second metal oxidation waves decreases to 110 mV for H1 and 60 mV in H2. This leads to significantly reduced $K_c$ values indicating a decreased interaction. This decrease in interaction upon protonation is even more prevalent for both H2H2 and H3H3 for which only a single two-electron oxidation wave is observed. This indicates that for the fully protonated species $K_c$ is less than 5 and that a mixed valence species does not form in detectable amounts.

More detailed information about the nature of this interaction can be obtained from spectroelectrochemical investigations. On the basis of the electrochemical results outlined previously, intervalence bands can be expected for the deprotonated and the singly protonated species. Analysis of the spectroscopic properties of the intervalence band allows for the estimate of the interaction parameter ($\alpha^2$) as in eq 319

$$\alpha^2 = \frac{(4.2 \times 10^{-4})\epsilon_{\max}V_{1/2}}{d^2E_{op}}$$

where $\epsilon_{\max}$ is the extinction coefficient of the IT band (M$^{-1}$ cm$^{-1}$), $V_{1/2}$ is its peak width at half-height, $d$ is the estimated metal to metal distance, 9.5 Å for these compounds, and $E_{op}$ is the energy of the absorption maximum of the intervalence band. Additional information can be obtained by estimating the theoretical peak width at half-height, $\Delta V_{1/2}$ calculated using eq 4.19

$$\Delta V_{1/2,\text{calcld}} = [2310(E_{op} - \Delta E)]^{1/2}$$

If the value of $\Delta V_{1/2}$ obtained from this equation correlates well with the value found from direct measurement, then the system can be described as valence localized RuIIRuIII, that is, Type II. If the IT band is narrower than the system, it is better described as type III (valence delocalized).20 The values obtained from eqs 1–4 are presented in Table 2. On the basis of these data and, in particular, because $\Delta V_{1/2}$ observed is larger than $\Delta V_{1/2,\text{calcld}}$, it seems clear that the mixed valence compounds behave as type II (or valence trapped) dinuclear species. Another important observation is that the $\Delta E$, $E_{op}$, and $\alpha^2$ values obtained for 1 and 2 are the same within experimental error (Table 2). This observation and the similarity of the energies of the LMCT bands observed for the mixed valence compounds indicate that LUMO of the bridging ligand plays at best minor roles in determining intercomponent interaction. Instead, it is expected that interaction between the metal centers is taking place via a hole transfer mechanism involving the HOMO of the metal units and bridging ligand.6 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 dπ-metal orbitals (metal based HOMO) and the σ-orbitals of the bridge.21 The spectroscopic and electrochemical data show that the ligand based σ-orbitals are stabilized upon protonation, so that the energy gap between the relevant orbitals increases, leading to decreased superexchange-assisted electronic interactions.

The $\alpha^2$ values given in Table 2 indicate that the amount of electron delocalization in 1 and 2 is considerably less than that observed in 3 and 4. This observation can be explained


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**Table 2. Spectroelectrochemical Data for Complexes 1–4 in 0.1 M TEAP/Acetonitrile**

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Delta E + 10$ mV</th>
<th>$K_c$</th>
<th>$\Delta_{\nu_{1/2,\text{calcld}}}$ (cm$^{-1}$)</th>
<th>$\Delta_{\nu_{1/2}}$ (cm$^{-1}$)</th>
<th>$\epsilon_{\text{max}}$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$E_{op} + 100$ cm$^{-1}$</th>
<th>$\alpha^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>180</td>
<td>1100</td>
<td>3060</td>
<td>4690</td>
<td>1820</td>
<td>5490</td>
<td>0.007</td>
</tr>
<tr>
<td>H1</td>
<td>110</td>
<td>72</td>
<td>4250</td>
<td>5600</td>
<td>1000</td>
<td>8700</td>
<td>0.0025</td>
</tr>
<tr>
<td>2</td>
<td>170</td>
<td>75</td>
<td>3120</td>
<td>4360</td>
<td>1120</td>
<td>5580</td>
<td>0.004</td>
</tr>
<tr>
<td>H2</td>
<td>60</td>
<td>10</td>
<td>4300</td>
<td>5300</td>
<td>1000</td>
<td>8500</td>
<td>0.0025</td>
</tr>
<tr>
<td>3*</td>
<td>300</td>
<td>117910</td>
<td>3341</td>
<td>3300</td>
<td>2400</td>
<td>5556</td>
<td>0.016</td>
</tr>
<tr>
<td>4*</td>
<td>300</td>
<td>117910</td>
<td>3260</td>
<td>4200</td>
<td>2200</td>
<td>5405</td>
<td>0.019</td>
</tr>
</tbody>
</table>

* Taken from ref 6. b Taken as double the width at half maximum of the high energy side of the absorption band.
by considering the difference in the distance between the two metal centers. Crystallographic data have shown that $d$ in 3 is 6.5 Å, while preliminary molecular modeling suggests that in 1 and 2 this distance is 9.5 Å. An additional factor may be that in 3 and 4 the negative charge of the bridge is shared between the two metal centers, while in 1 and 2 the triazole based negative charge is expected to be more localized.

Finally, the difference in the redox and luminescence properties of the deprotonated (1 and 2), monoprotonated (H1 and H2), and the diprotonated (H21 and H22) species warrants some additional comments. On looking at Table 1 and Figure 5, it is clear that the luminescence output of 1 can be switched between three “states” in terms of emission energy and lifetime. It should be stressed, however, that the excited-state responsible for the emission remains the same in all three cases. So, the behavior observed cannot be explained by a switching process between different electronic states. It is rather a stepwise protonation, which perturbs the emitting excited state in such a way that three different outputs are generated. In principle, the same also occurs for 2; however, the changes in luminescence energy are almost negligible. While the switching of the luminescence output between two “states” is common,12 the possibility of switching luminescence between three different outputs is less so. In addition, the redox properties of both compounds can also be employed in this respect. For example, by monitoring of the current at 0.8, 1.05, and 1.15 V, the protonation state of 1 may be “read”. In view of the future development in the design of systems capable of manipulating information (e.g., light or electrons) at the molecular level, our results offer new lines toward this goal, in terms of both synthetic methods and physical properties.

Conclusions

With the ever-increasing interest in multinuclear metal complexes as supramolecular systems, the assemblies investigated are becoming ever more complex. As a result, the formation of isomers and side products is an increasing problem. The Ni(0) catalyzed homonuclear coupling reported in this contribution is simple and leads to pure compounds in a high yield, in cases where direct reaction of the bridging ligand with the metal centers leads to a mixture of products.22 To the best of our knowledge, this is the first time such a coupling has been carried out with ruthenium(II) polypyridyl complexes.8 The method can be adapted to many other systems and constitutes, therefore, together with some related methods, an important tool for the design of novel supramolecular assemblies.

The electrochemical and photophysical studies of the dinuclear compounds obtained illustrate the “tunable nature” of the properties of these supramolecular systems and their potential as molecular switches. The close proximity of the two triazole rings creates interaction between the two parts of the molecule, and the three protonation states obtained show different levels of intercomponent interaction. It is, furthermore, important to note that while the differences in ground-state properties and metal—metal interaction between the pyridine (1) and pyrazine (2) based complexes are minor, their luminescence properties are substantially different. Relatively small changes in the composition of the compounds, that is, pyridine versus pyrazine, lead to compounds with different excited-state properties. Taking into account the synthetic procedures used in this investigation, this opens the possibility for extensive variation in the components that can be used to build up a range in proton gated redox active and emitting compounds.

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