Photoinduced ligand transformations in a ruthenium complex of dimethoxytetrapyridoditetrarazapentacene

Shreemukta Singh, Norma R. de Tacconi, David Boston and Frederick M. MacDonnell*

Received 7th August 2010, Accepted 16th September 2010
DOI: 10.1039/c0dt00982b

The dinuclear ruthenium(II) complex \([\text{phen}]_2\text{Ru(tatpOMe)}\text{Ru(phen)}_2\)]^4+ (2^4+; phen is 1,10-phenanthroline and tatpOMe is 10,21-dimethoxy-9,10,20,33-tetraazatetrapyrido[3,2-a:2'-c:3'-2'-l:2'-n]pentacene) has been synthesized and characterized by 1H NMR, ESI mass spectroscopy and elemental analysis. Loss of methoxy group from bridging ligand of complex 2^4+ due to irradiation is observed by 1H NMR and photochemistry. The interrelated electronic properties UV-Vis, electrochemistry, photochemistry and molecular orbital calculation are analyzed and discussed on the bridging ligand of the complex 2^4+.

Introduction

Ruthenium(II) polypyridyl complexes continue to enjoy considerable attention as chromophores for molecular light-to-chemical energy conversion schemes.1-4 The development of molecular photocatalysts capable of driving conversion of common substrates into fuels, i.e. \(\text{H}^+\) into \(\text{H}_2\) and \(\text{CO}_2\) into \(\text{CH}_3\text{OH}\), needs to address the multi-electron requirements of the substrates and still couple this with the single-photon, single-electron excitation common for most chromophores. One strategy has been to build photocatalysts capable of photodriven multi-electron storage, such that they absorb multiple photons over time and build-up reducing (or oxidizing equivalents) within their structure. Brewer and co-workers were first to demonstrate this in 1994 in a trimetallic Ru–Ir–Ru complex which was later extended to Ru–Rh–Ru systems.5-7 In the latter Rh-based system, photon absorption by the Ru components drives a Rh(III/I) reduction and this center is subsequently able to reduce protons to \(\text{H}_2\); A number of other molecular8-11 and supramolecular12-15 Ru–Pt or Ru–Pd bimetallic systems have also been shown to produce \(\text{H}_2\) photochemically in the presence of sacrificial donors.

We have been exploring the photochemistry of ruthenium complexes, shown in Fig. 1, containing a unique class of planar aromatic acceptor ligands related to the well-known dppz ligand. Mononuclear and dinuclear ruthenium(II) complexes of the tetraazatetrapyridophenazine (tatpp) ligand display unusual photochemical activity in which the tatpp ligand is reduced by up to 2 electrons upon visible light irradiation in the presence of sacrificial donors.16-19 The dinuclear ruthenium complex, \([\text{phen}]_2\text{Ru}^{II}(\text{tatpp})\text{Ru}^{II}(\text{phen})_2\)]^4+, has also been shown to bind DNA via intercalation and cleave DNA in a process that is enhanced under low oxygen conditions.20 The closely related complex, \([\text{phen}]_2\text{Ru}^{II}(\text{tatpq})\text{Ru}^{II}(\text{phen})_2\)]^4+, 3^4+, is also photochemically active and can undergo up to four tatpq ligand-based reductions via photon driven processes.19,21

While both 1^4+ and 3^4+ can photochemically store multiple electrons reversibly on the bridging ligands, neither complex has shown much promise as for solar \(\text{H}_2\) generation owing to the modest reduction potentials of these stored electrons. In this work, we explore the substitution of the central hydrogens in tatpp with methoxy electron-donating groups (tatpOMe) in an effort to shift the reduction potentials of the resulting ruthenium complex, \([\text{phen}]_2\text{Ru}^{II}(\text{tatpOMe})\text{Ru}^{II}(\text{phen})_2\)]^4+ (2^4+), to more negative values. If this complex retains the photochemical activity of the parent tatpp complex, then we could aim to photoreduce this new complex by 2-electrons and potentially store them at more negative reduction potentials. In this report, we describe the synthesis and characterization of the tatpOMe ligand and its dinuclear ruthenium(II) complex, as well as an evaluation of

Fig. 1 Structures of dinuclear ruthenium(II) complexes having central bridging ligand tatpp, tatpOMe and tatpq.
of its electrochemical and photochemical properties for use as a photocatalyst for photon-driven multi-electron storage and transfer.

**Experimental**

**Chemicals**

The compounds 1,10-phenanthroline (phen), hydrated ruthenium(II)chloride, p-benzoquinone, toluensulfonyl-chloride were purchased from Aldrich or Alfa and used without further purification. Ru(phen)_2Cl_2, 2, 11,10-Phenanthroline-5,6-dione (phenodione), 23 1,4-dimethoxy-2,3-dinitrobenzene, 24 1,2-dianilino-3,6-dimethoxybenzene 24 were prepared according to literature procedures. All organic solvents were of analytical grade and used as received unless stated otherwise. For electrochemical measurements, the acetonitrile (MeCN, Aldrich) was dried on alumina and distilled under nitrogen prior to use. The supporting electrolyte Bu_4NPF_6 (Aldrich) was dried overnight under vacuum prior to use. The supporting electrolyte Bu_4NPF_6 (Aldrich) was dried overnight under vacuum prior to use. The supporting electrolyte Bu_4NPF_6 (Aldrich) was dried overnight under vacuum prior to use.

**Physical Measurements**

^1H and ^13C NMR spectra were obtained on a JEOL Eclipse Plus 500 or 300 MHz spectrometer using CDCl_3 as the solvent unless otherwise noted. Chemical shifts are given in ppm and referenced to TMS. UV-Visible spectra were obtained on a Hewlett-Packard HP8453A spectrophotometer in MeCN.

**Photochemical Reaction**

The UV-Visible spectra were obtained using a Hewlett-Packard HP8453A spectrophotometer. All solutions were sealed in a quartz cuvette and degassed for 10 min with nitrogen prior to irradiation. The cuvettes were irradiated using 150 W halogen lamp (StockerYale Imageelite Model 21AC) clear glass, light bulb. The progress of the photochemical reaction was monitored by recording the absorption spectra. All absorption measurements were done at room temperature using a sample concentration of 16 μM dissolved in MeCN.

**Electrochemistry**

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were conducted in dry acetonitrile (Aldrich, 99.93%, HPLC grade) with 0.1 M NBut_4PF_6 (Sigma) as supporting electrolyte using a CH600C electrochemical analyzer (CH Instruments). A glassy carbon disc (1.5 mm diameter disk, Cypress Systems) was used as working electrode in conjunction with a Pt wire and a premium “no leak” Ag/AgCl/3M KCl (Cypress, model EE009) as counter and reference electrode respectively. Potentials are quoted with respect to NHE. Oxygen was exhaustively removed from the electrochemical cell by bubbling purified nitrogen.

**Molecular Orbital Calculations**

The molecular and electronic structure calculations for 1^+ and 2^+ were performed with density functional theory (DFT) using the Gaussian03 program package using the B3LYP functional. 23 A cc-pVDZ basis set was used for hydrogen, carbon, nitrogen, and a LanL2DZ basis set for ruthenium. Solvent effects were modeled by single-point calculations based on the gas phase optimized structures using the polarizable continuum model (PCM). The orbital analysis was completed with Gaussview.

**Synthesis**

3,6-dimethoxybenzene-4,5-bis(p-toluenesulfonamido)benzene. To a solution of 5.0 g (0.03 mmol) 1,2-diamino-3,6-dimethoxybenzene 23 dissolved in 10 mL pyridine was added 3 equivalents (9.6 g, 0.09 mmol) of p-toluensulfonyl chloride in three portions. The resulting solution was heated to 35 °C for 2 h. and then poured into a large beaker containing 1000 mL H_2O. The resulting precipitate was filtered and recrystallized from ethanol. Yield: 13 g (92%). M.p. 125–128 °C. ^1H NMR (CDCl_3) δ = 2.39 (s, 6H), 3.39 (s, 6H), 6.59 (s, 2H, NH), 6.96 (s, 2H), 7.20 (d, J_HH = 8.1 Hz, 4H), 7.58 (d, J_HH = 8.1 Hz, 4H).

4,5-Dinitro-3,6-dimethoxy-4,5-bis(p-toluenesulfonamido)benzene. 3,6-Dimethoxybenzene-4,5-bis(p-toluenesulfonamido)benzene (10 g, 20.9 mmol) was dissolved in 15 mL of acetic acid and heated to 60 °C. A mixture of fuming nitric acid (4 mL) acetic acid (2 mL) was slowly added to the first solution and then refluxed for 1 h at 100–110 °C. The resulting solution was poured into a large beaker containing 1000 mL water. The resulting precipitate was isolated by filtration and recrystallized from ethanol. Yield: 10.7 g (90%). M.p. 122–125 °C. ^1H NMR (CDCl_3) δ = 2.45 (s, 6H), 3.44 (s, 6H), 7.25 (s, 2H, NH), 7.34 (d, J_HH = 8.1 Hz, 4H), 7.74 (d, J_HH = 8.1 Hz, 4H).

1,2-Diamino-3,6-dimethoxy-4,5-bis(p-toluencesulfonamido)benzene. 4,5-Dinitro-3,6-dimethoxy-4,5-bis(p-toluencesulfonamido)benzene (1.0 g, 1.8 mmol) and 10% Pd on C (30 m) were suspended in 20 mL ethanol in a steel pressure reactor. The resulting mixture was hydrogenated for 24 h. at room temperature at 5 bar H_2. After cooling and venting, the reaction mixture was filtered using Celite and the resulting solution concentrated to dryness using a rotatory evaporator to yield a pink colored crystalline product. Yield 0.70 g (80%). M.p. 86–90 °C. ^1H NMR (CDCl_3) δ = 2.38 (s, 6H), 3.48 (s, 6H), 7.25 (s, 2H, NH), 7.19 (d, J_HH = 8.1 Hz, 4H), 7.56 (d, J_HH = 8.1 Hz, 4H).

10,13-dimethoxy-11,12-bis(p-toluensulfamido)-dipyrido[3,2-a']2,3'-clphenazine. 1,2-Diamino-3,6-dimethoxy-4,5-bis(p-toluencesulfonamido)benzene (100 mg, 0.19 mmol) and 1,10-phenanthroline-5,6-dione (21.7 mg, 0.18 mmol) were suspended in 50 mL of ethanol and refluxed for 6 h. The solution was filtered hot and the precipitate washed with ethanol and dried under vacuo. Yield 130 mg (98%). M.p. 130–132 °C. ^1H NMR (CDCl_3) δ = 2.40 (s, 6H), 3.99 (s, 6H), 7.27 (d, J_HH = 8.1 Hz, 4H), 7.54 (s, 2H, NH), 7.73 (d, J_HH = 8.1 Hz, 4H), 7.78 (dd, J_HH = 9.0 Hz, 2H), 9.28 (d, J_HH = 6.0 Hz, 2H), 9.45 (d, J_HH = 9.0 Hz, 2H).

11,12-Diamino-10,13-dimethoxy-dipyrido[3,2-a':2',3'-c]phenazine. Detosylation of 10,13-dimethoxy-11,12-bis(p-toluencesulfamido)-dipyrido[3,2-a':2',3'-c]phenazine (1 g, 1.4 mmol) was accomplished by dissolving the solid in 15 mL concentrated sulfuric acid and then heating this solution to 80 °C for 4 h in a water bath. The resulting dark violet solution was then added dropwise to ice water and filtered. The resulting filtrate was treated with a saturated solution of NaHCO_3 until the pH was ~6 to 7, during which the free diamine precipitated from solution.
The product was isolated by filtration and dried. Yield 0.37 g (68%), M.p. 128–130 °C. 1H NMR (CDCl₃) δ = 4.14 (s, 6H), 7.95 (dd, JHH = 9.0 Hz, 2H), 9.28 (d, JHH = 6.0 Hz, 2H), 9.65 (d, JHH = 9.0 Hz, 2H).

10,21-Dimethoxy-9,10,20,33-tetraazatetrapyrido[3,2-a':2',3',2'-t2',3'-c]pentacene (tatpOMe). 11,12-Diamino-10,13-dimethoxy-dipyrido[3,2-a',3'-c]phenazine (100 mg, 0.26 mmol) and 1,10-phenanthroline-5,6-dione (5.6 mg, 0.26 mmol) were dissolved in 15 mL acetic acid and refluxed overnight, during which time a precipitate formed. After cooling the reaction mixture filtered and the solid washed with 100 mL water. Yield 121 mg, (92%), M.P . 190–192 °C. Anal. Calc. For C₃₂H₁₈N₈O₂: C, 70.32; H, 3.32; N, 20.50. Found: C, 70.02; H, 3.15; N, 20.39. 1H NMR (CDCl₃) δ = 4.88 (s, 6H), 7.84 (dd, JHH = 9.0 Hz, 2H), 9.32 (d, JHH = 6.0 Hz, 2H), 9.70 (d, JHH = 9.0 Hz, 2H). 13CN M R (CDCl₃) δ: 65.3, 124.5, 127.5, 134.0, 134.5, 141.9, 147.7, 149.1, 153.3.

[(phen)₂Ru(tatpOMe)Ru(phen)₂][PF₆]₄. All procedures for this synthesis were conducted under anaerobic and low-light conditions. The reaction vessel was wrapped in aluminium foil during the reflux period to avoid light exposure. TatpOMe (100 mg, 18 mmol) and Ru(phen)₂Cl₂ (90 mg, 0.18 mmol) were suspended in a chloroform–ethanol (50 : 50) mixture under a N₂ atmosphere. The resulting slurry was refluxed for 1 day after which a second 90 mg (0.18 mmol) portion of Ru(phen)₂Cl₂ was added. The resulting solution was refluxed for a total of 8 days and then filtered hot and most of the chloroform removed by rotary evaporation. Addition of an aqueous solution of NH₄PF₆ to the ethanol solution results in the formation of a precipitate which is isolated by filtration and washed with 10 mL of chloroform. This product is further purified by metatheses between the Cl⁻ and PF₆⁻ salts in dark. Yield: 240 mg (64%). Anal. Calc. For C₈₀H₅₀F₂₄N₁₆O₂P₄: C, 46.89; H, 2.46; N, 10.49. Found: C, 46.42; H, 2.38; N, 10.52. 1H NMR (CDCl₃) δ = 4.81 (s, 6H), 7.64–7.84 (dd, JHH = 9.0 Hz), 8.1 (d, 1H), 8.22 (d, 1H) 8.26 (s), 8.61 (apparent triplet) 9.64 (d, JHH = 9.0 Hz, 2H). ESI-MS (m/z): 1906 [3⁺-PF₆]⁺, 879.67 [3⁺-2PF₆]⁺2, 538.67 [3⁺-3PF₆]⁺³, 367.87 [3⁺]⁴⁺.

Results and discussion

Synthesis

The complete synthetic route followed for preparation of the ligand, tatpOMe, and the dinuclear ruthenium(II) complex, [(phen)₂Ru(tatpOMe)Ru(phen)₂][PF₆]₄, is shown in Fig. 2. The amine functions on 1,2-diamino-3,6-dimethoxybenzene are protected by tosylation and the dinitro compound formed by treatment with fuming nitric acid and sulfuric acid to obtain 4,5-dinitro-3,6-dimethoxy-4,5-bis(p-toluenesulfonamido)benzene following the methods developed by Starns et.al. for the non-methoxylated compound. This compound is converted to the diamine by reduction with H₂ over a Pd/C catalyst. The resulting 1,2-diamino-3,6-dimethoxy-4,5-bis(p-toluenesulfonamido)benzene is coupled with one equivalent of 1,10-phenanthroline-5,6-dione to give the bis N-tosylated dppz ligand.

![Fig. 2](https://example.com/fig2.png)

Fig. 2 Synthesis of tatpOMe and [(phen)₂Ru(tatpOMe)Ru(phen)₂][PF₆]₄.
After detosylation, the resulting 11,12-diamino-10,13-dimethoxy-dipyrro[3,2-a:2’,3’-c]phenazine is coupled with one equivalent of 1,10-phenanthroline-5,6-dione to yield the dark brown colored ligand tatpOMe in 31% overall yield. Unlike the insoluble tatpp ligand, tatpOMe is slightly soluble in chloroform and dichloromethane, thereby allowing a straightforward NMR analysis of the highly symmetric structure (D₅h point group). The ¹H NMR of tatpOMe in CDCl₃ shows 4 peaks with a singlet for the -OMe groups at 3.88 ppm and the characteristic AMX splitting for the aromatic H₁, H₃, and H₆ in the 7–10 ppm region. The proximity of H₁ to the pyrazine nitrogen lone pairs causes a distinctive downfield shift in related compounds and is seen here at 9.70 ppm. Elemental analysis data also support the proposed structure.

The dinuclear ruthenium(II) complex, [[(phen)₂Ru-(tatpOMe)Ru(phen)][PF₆]₄], is prepared by a prolonged refluxing of the slightly soluble tatpOMe ligand with 2 equivalents of Ru(phen)₂Cl₂ in 1:1 chloroform-ethanol. As expected, the ¹H NMR spectrum of [(phen)₂Ru(tatpOMe)Ru(phen)][PF₆]₄ (in deuterioacetonitrile) is very similar to that of [[PF₆]₄. The notable differences being the large singlet at 4.81 ppm for the two methoxy groups in 2⁺ and the absence of the peak corresponding to central hydrogens in tatpp. The H₂ protons of the tatpOMe ligand are observed the most downfield in 2⁺ at 9.64 ppm, which is in a similar range as the similarly situated protons in 1⁺ at 9.70 ppm and 3⁺ at 9.68 ppm. A complete spectrum and peak assignment are given in the supporting information.

Electrochemistry

The redox properties of the tatpOMe in CH₂Cl₂ and complex 2[PF₆]₄ in MeCN were analyzed by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) and the data are collected in Table 1 along with that for complex 1[PF₆]₄. The redox data provides information regarding the frontier molecular orbital energies of the free tatpOMe ligand and the complex 2⁺. All of the electron transfer processes for the tatpOMe ligand are irreversible and therefore peak potentials (instead of half-wave potentials) obtained from DPV data are listed for the free ligand in Table 1. The first oxidative process at +1.21 V reveals that the energy of the tatpOMe HOMO is below that typically found for metal-based HOMO typical of [Ru(phen)]³⁺ and closely related derivatives whose potential is approximately +1.5 V vs. NHE. On the other side, the ligand LUMO is shown to be accessible at a potential of ~0.24 V by DPV. It is an irreversible process and is indicative of significant structural changes in the ligand upon reduction, which we now know to be associated with loss of the methoxy or methoxy functions (vide infra).

In the dinuclear ruthenium(II) complex 2⁺, a total of four redox processes are observed in the DPV data shown in Fig. 3. The reversible redox process centered at +1.58 V is assigned to the two Ru²⁺³⁻ couples. As seen with complex 1⁺ at +1.60 V, the two one-electron couples occur as a single peak indicating the two Ru(II) centers are sufficiently far apart that electronic coupling is negligible. The remaining three electrochemical processes of complex 2⁺ are associated with reduction or oxidation of the coordinated tatpOMe ligand (Fig. 3). An irreversible oxidative process at +1.31 V is associated with a tatpOMe⁰⁺⁺ couple which is shifted positive by 100 mV relative to the same process in the free ligand at +1.21 V (see Table 1). The positive shift is attributed to the increase in overall charge upon complex formation.

In the dinuclear ruthenium(II) complex 2⁺, a total of four redox processes are observed in the DPV data shown in Fig. 3. The reversible redox process centered at +1.58 V is assigned to the two Ru²⁺³⁻ couples. As seen with complex 1⁺ at +1.60 V, the two one-electron couples occur as a single peak indicating the two Ru(II) centers are sufficiently far apart that electronic coupling is negligible. The remaining three electrochemical processes of complex 2⁺ are associated with reduction or oxidation of the coordinated tatpOMe ligand (Fig. 3). An irreversible oxidative process at +1.31 V is associated with a tatpOMe⁰⁺⁺ couple which is shifted positive by 100 mV relative to the same process in the free ligand at +1.21 V (see Table 1). The positive shift is attributed to the increase in overall charge upon complex formation.

**Table 1** Electrochemical data for [(phen)₃Ru(tatp)Ru(phen)₃]⁺⁺ and [(phen)₃Ru(tatpOMe)Ru(phen)₃]⁺⁺ in acetonitrile and tatpOMe in CH₂Cl₂

<table>
<thead>
<tr>
<th></th>
<th>Oxidation/V*</th>
<th>Reduction/V*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st</td>
<td>2nd</td>
</tr>
<tr>
<td>[(phen)₃Ru(tatp)Ru(phen)₃]⁺⁺ (in MeCN)</td>
<td>1.21 (ir)</td>
<td>1.43 (ir)</td>
</tr>
<tr>
<td>tatpOMe (in CH₂Cl₂)</td>
<td>1.31 (ir)</td>
<td>1.60 (2)</td>
</tr>
<tr>
<td>[(phen)₃Ru(tatpOMe)Ru(phen)₃]⁺⁺ (in MeCN)</td>
<td>1.21 (ir)</td>
<td>1.43 (ir)</td>
</tr>
</tbody>
</table>

* Potentials were measured vs. Ag/AgCl/3M KCl reference electrode and converted to NHE by adding 0.197 V. Number of electrons is shown in parenthesis and irreversible processes are indicated with "ir".

**Fig. 3** DPV runs on a glassy carbon electrode (1.5 mm diameter) for 80 μM [2[PF₆]₄] in acetonitrile containing 0.1 M TBAPF₆ as supporting electrolyte. Four individual runs are shown encompassing the potential windows for reduction (0.4 V–0.9 V) and oxidation (0.4 V–1.9 V) processes respectively. Each potential window was scanned in positive- and negative-going potential direction. Pulse amplitude = 0.01 V, step size = 0.001 V, pulse duration = 0.05 s, and pulse period = 0.2 s.

Complex 1⁺ does not show a tatpp⁰⁻¹ couple prior to the Ru²⁺³⁻ (see Table 1) indicating that the HOMO of coordinated tatpp is lower in energy than that for coordinated tatpOMe. It seems that the electron-donating methoxy groups destabilize the tatpOMe

**Dalton Trans.**

This journal is © The Royal Society of Chemistry 2010
HOMO relative to tatpp such that it becomes the HOMO for the overall complex.

The two redox processes of complex 2+ at −0.05 V and −0.52 V are certainly associated with the reduction of the coordinated tatpOMe ligand because the reductions associated with the terminal phen groups are known to require reduction potentials more negative than −1.2 V. These reductions occur at potentials nearly identical with those for 1+ but unlike the 1+/-2+ and 1+/-3+ couples which are of similar shape and intensity, these two reductions show very different peak areas and intensities as shown in Fig. 3. The magnitude of the process at −0.52 V is unusually large, even larger than the 2-electron Ru2+/3+ couple, suggesting a multi-electron process. On the other hand, the magnitude of the first reductive couple at −0.05 V is less than half the intensity of the Ru2+/3+ couple. As these processes appear to be mostly reversible, it seems reasonable to assign the −0.05 V process to a tatpOMe3/-2 couple whereas the larger peak at −0.52 V process is indicative of a multi-electron transfer process with at least 2 electrons. It is also noteworthy that the irreversible reductive process observed for the free tatpOMe ligand at −0.24 V is now shifted to −0.05 V for the respective tatpOMe3/-2 couple in 2+ because of the effect of Ru(tatpp) coordination.

Electronic Absorption Spectroscopy

The electronic absorption spectra for the free tatpOMe ligand in CHCl3, the Zn(tatpp) adduct of tatpOMe in MeCN, and the Zn(tatpp) adduct of tatpp in MeCN are shown in Fig. 4 and the respective absorption bands are compiled in Table 2. The free tatpOMe ligand is generally insoluble but can be dissolved in MeCN upon addition of a 5–10 fold molar excess of Zn(BF4)2, presumably due to formation of the bis Zn(tatpp) adduct. As tatpOMe is soluble in CHCl3, both the free ligand spectrum and that of its Zn(tatpp) adduct in MeCN are compared in Fig. 4. The free tatpOMe in CHCl3 shows an intense LC transition at 350 nm and weaker structured LC transitions with distinct peaks at 410 nm, 434 nm, and 461 nm. The spectrum of the Zn(tatpp)-tatpOMe adduct is very similar to that of tatpOMe except that the structured peaks are shifted to higher energy at 405, 430, and 457 nm upon coordination to the Zn(tatpp) ions. This blue shift is likely due to stabilization of the tatpOMe HOMO upon coordination to the electron withdrawing and positively charged Zn(tatpp) ions. By comparison, the Zn(tatpp)-tatpp adduct also shows two strong peaks:

![Absorption spectra of the free tatpOMe ligand in CHCl3, the tatpOMe ligand in MeCN with 10 eq Zn(BF4)2, and the tatpp ligand in MeCN with 10 eq Zn(BF4)2.](image)

Fig. 4 Absorption spectra of the free tatpOMe ligand in CHCl3, the tatpOMe ligand in MeCN with 10 eq Zn(BF4)2, and the tatpp ligand in MeCN with 10 eq Zn(BF4)2.

Table 2: Absorption data of the dinuclear ruthenium complexes and Zn(tatpp) adducts of tatpp, tatpOMe and in MeCN

<table>
<thead>
<tr>
<th>Compound</th>
<th>abs, 298 K: λmax, nm (ε x 10^4, M⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(phen)2Ru(tatpp)Ru(phen)2][PF6]4</td>
<td>444 (6.30), 422 (4.91), 396 (3.70), 323 (8.48)</td>
</tr>
<tr>
<td>[(phen)2Ru(tatpq)Ru(phen)2][PF6]4</td>
<td>441 (3.60), 370 (4.57), 318 (5.16)</td>
</tr>
<tr>
<td>[(phen)2Ru(tatpOMe)Ru(phen)2][PF6]4</td>
<td>448 (4.20), 430 (4.04), 350 (9.03)</td>
</tr>
<tr>
<td>tatppOMe (in CH2Cl2)</td>
<td>462 (1.26), 434 (0.861), 410 (0.513)</td>
</tr>
<tr>
<td>Zn-tatppOMe adduct</td>
<td>456 (1.01), 430 (0.934), 405 (0.809)</td>
</tr>
<tr>
<td>Zn-tatpp adduct</td>
<td>448 (1.75), 423 (1.30), 400 (0.460), 380 (0.460), 323 (4.57)</td>
</tr>
</tbody>
</table>

An intense transition at 323 nm and a structured transition with peaks at 400, 423, and 447 nm. Given the close structural similarity of the tatpp and tatpOMe ligands and the similarity of their absorption spectra, it seems reasonable to assume isoelectronic transitions are occurring in both ligands. From previous studies of the tatpp ligand, we have assigned the lowest energy transition in both ligands as a π(πHOMO)→π*(LUMO) transition and the higher energy transition at 323 nm as a π(πHOMO)→π*(LUMO+1) transition. All of the ligand-centered transitions in tatpp are observed at higher energy than the isoelectronic transitions in tatpOMe. Given the electrochemical data (Fig. 3) and this red shift in peaks for tatpOMe (Fig. 4), it is reasonable to assume that the methoxy substituents destabilize the ligand HOMO with respect to the original tatpp moiety.

The electronic absorption spectra of the ruthenium complexes 1+, 2+, and 3+ in MeCN are shown in Fig. 5 and their absorption bands are reported in Table 2. The spectra for 1+ and 2+ are similar excepting for the intensity of the transitions in the 410–450 nm region. The spectrum of 1+ was shown to be comprised of two overlapping bands (the MLCT and structured LC band) in the 410–450 nm region which is also apparent in 2+ with the lower intensity being due to the lower extinction coefficient for the LC transition in tatpOMe in this region. The MLCT band for 1+ and 2+ peaks at ~ 450 nm and is associated with a Ru(tatpp) π→π({π}) transition that occurs at virtually the same energy as seen for [Ru(phen)]^2+. This transition can be assigned to Ru(tatpp) π→π({π}) in 1+ and 2+ both of which also show broad lower energy shoulders between 500 and 600 nm. These broad and

![Electronic absorption spectra of the 1+, 2+, and 3+ (16 μM) in acetonitrile.](image)

Fig. 5 Electronic absorption spectra of the 1+, 2+, and 3+ (16 μM) in acetonitrile.
moderately intense, low-energy transitions are likely to be MLCT bands associated with the tatpp and tatpOMe ligands, which have low energy π* orbitals as indicated by their redox properties. The degree of electronic coupling of these low energy ‘redox orbitals’ with the Ru dπ HOMO has been the subject of considerable study in these and related dppz and tpphz complexes.28,32–39

For dppz28,32–34 and tpphz,35–39 it has been shown that two acceptor orbitals play significant roles in the overall complexes behavior. The ‘redox orbital’ is the lowest lying ligand MO and is the first MO populated upon chemical or electrochemical reduction. The ‘optical orbital’ is a MO with acceptor characteristics energetically and symmetrically similar to the LUMO on a bipyridine ligand and is usually the LUMO+1 for dppz or tpphz when coordinated to Ru(II). This ‘optical orbital’ is the MO populated upon excitation into the complex MLCT band at ca. 480 nm. For tpphz and dppz, the electronic absorption spectra do not show any significant absorptions below this 480 nm band and thus it appears that the oscillator strength for the Ru(II) dπ → dppz (or tpphz) π*(LUMO) is very small or zero. This has been explained by MO calculations which show little or no π orbital density on the coordinated nitrogens for the LUMO.28,35–39 Similar arguments have been made for the tatpp and tatpq ligands.29

Molecular Orbital Calculations

In order to interpret and compare the electrochemical and optical data for 1+ and 2+, MO calculations were performed on the structures using DFT theory as described in the experimental section. Fig. 6 shows the energy, orbital density, and symmetry for the relevant frontier orbitals on 1+ and 2+. For both 1+ and 2+, the LUMO+1 MOs (π*) were identified as having ‘bipyridine-like’ orbital symmetry and density on the tatpp or tatpOMe ligands.

The energy of these two π* MOs was arbitrarily set to zero for subsequent comparisons. The LUMOs (π0) for 1+ and 2+ were both approximately 1 eV lower than the π* MOs and showed large orbital density on the central portions of the ligands and little or no orbital density on the nitrogens coordinated to the Ru(II) ions, which is similar to the situation observed in dppz and tpphz complexes. The highest occupied MOs with Ru dπ character in both complexes have nearly equal energies of ca. -3.6 eV relative to the π* however the relative order of MO’s has now changed. This Ru dπ orbital corresponds to the HOMO for 1+ and is the HOMO-1 for 2+. The HOMO for 2+ is largely localized on the central portion tatpOMe ligand and thus the first ‘redox orbital’ that should be accessed during the oxidation of the 2+ is a ligand-centered MO. This description corresponds nicely with the electrochemical data in which an irreversible oxidation peak was seen at +1.32 V prior to the Ru2+/3+ couple at +1.54 V in the DPV of 2+. We had assigned this oxidation to the coordinated tatpOMeπ+ coupling and can show it is irreversible because tatpOMe oxidation or reduction has been found to lead to demethylation or demethoxylation (vide infra).

On the other hand, the tatpp complex 1+ does not show a ligand-centered occupied MO until the HOMO-6, indication that the first oxidative process seen electrochemically should be the Ruπ+/2+ couple which is what is observed at +1.54 V. The intervening orbitals, HOMO-1 to HOMO-5, are all related to the Ru dπ orbitals. From these data and calculations, we can now see that the largest impact of replacing the hydrogens in tatpp with methoxy functions in tatpOMe is to raise the energy of the ligand HOMO, in this case to something above the Ru dπ orbitals. A similar effect is seen in the LUMO’s for 1+ and 2+ with the energy of the LUMO for 2+ being found at higher energy than the LUMO for 1+, however the magnitude of the effect is much less significant on the unoccupied orbitals.

The broad shoulder observed in the optical spectra of 1+ and 2+ between 500 and 600 nm is not observed in either spectrum of the Zn(II) adducts of respective ligands in MeCN ruling out a LC type transition. Similarly, this shoulder is not observed in the spectrum of [Ru(phen)]. The two observations, the broadness of the shoulders, plus the appreciable extinction coefficients (ca. 10,000 M-1 cm-1 for 1+ and 6,000 M-1 cm-1 for 2+) are suggestive of MLCT type transitions involving the tatpp or tatpOMe ligands. From the MO picture, two types of MLCT’s are possible; a MLCT involving a Ru dπ → π* (MLCT0) transition or a Ru dπ → π* (MLCT1). There are two reasons we favor the latter transition as the origin of the shoulder in 1+ and 2+. First, the MO calculations show no π orbital density on the coordinated nitrogens in the π* orbital of 1+ and 2+. The analogous MLCT1

Fig. 6  MO energy diagram of the relevant frontier molecular orbitals for complexes 1+ and 2+.
transition in Ru(ttt)dpdz and Ru(ttt)tpphz complexes, which have very similar electronic structures, is not observed, therefore it is not expected in 14+ and 24+. Second, if the MLCT transition in 14+ and 24+ is observed at 450 nm, the nearly 1 eV drop in energy for the MLCT transitions would be expected to give peaks at wavelengths near 700 nm, which is much lower in energy than what is observed. If, however, the electronic origin of the shoulder is the MLCT transition, the spectra can be explained as follows: strong Ru dxπ → π* (phen) transitions occur around 450 nm and are overlapping with a broad Ru dπ → π* (phen) transition for tatpp and tatpOMe having a maxima closer to 510 nm. The energy of the π*, orbital in tatpp and tatpOMe is a little lower in energy than the phen π* orbital of similar symmetry due the electron withdrawing central portions of these ligands.

**Photochemistry**

The photochemical activity of complex 24+ was examined under similar conditions which resulted in multi-electron reduction of complexes 14+ and 34+. Irradiation of the complex in MeCN containing 0.25 M TEA under anaerobic conditions leads to the spectral evolution shown in Fig. 7. After 5 s irradiation, peaks appear at 878 and 1000 nm along with an increase in the intensity of the band at 450 nm. This is analogous the changes initially observed during the irradiation of 14+ under similar conditions and corresponds to the formation of the radical complex [(phen),Ru4(tatpOMe−)4Ru4(phen)4]4+ by MLCT excitation and reductive quenching with TEA. By 20 s, these two peaks at long wavelength are replaced by an intense peak at 1050 nm and increases the intensity of the 635 nm peak, supporting conversion of [(phen),Ru4(tatpq−)4Ru4(phen)4]4+ to [(phen),Ru4(tatpq4)4Ru4(phen)4]4+. No further changes are observed upon further irradiation, however, exposure of the final solution to air rapidly bleaches all peaks above 500 nm. The final spectrum mirrors that as seen for complex 34+ with dominant peaks at 444 nm and 370 nm and a shoulder at 315 nm. ESI-mass spectrometric analysis of this final solution reveals a dominant parent ion peak at 1872 m/z which corresponds to the m/z for {([phen],Ru(tatpq)Ru(phen)4)[PF6]+}.

From these data, it is clear that complex 24+ was converted to the quinone complex 34+ during the photochemical process and subsequent air oxidation. The evolution of the absorption data support demethylation of the methoxy substituents upon 1-electron reduction of the tatpOMe ligand in 24+. Melloni et al. have shown that the reductive cleavage of o-, m-, p-dimethoxybenzene ethers can be induced via potassium reduction under anaerobic conditions. Both demethylation or demethoxylation products are observed and are favored by one or two-electron reductions mechanisms, respectively. In this case, reductive quenching of the 3MLCT state in 24+ traps a single electron on the tatpOMe ligand favoring demethylation.

We also noted that complex 24+ appeared to be sensitive to photochemical degradation in the absence of sacrificial donors. Irradiation of 24+ with visible light in anaerobic MeCN solution, leads to a nearly complete bleaching of the tatpOMe LC peaks leaving only the broad Ru dxπ → π* (phen) type MLCT at 450 nm and no new absorptions at longer wavelengths. Exposure of this unknown intermediate to air does not return the spectrum to its original 24+ but instead results in a spectrum which has features of both 14+ and 34+ complex with peaks at 315 nm, 370 nm, and a structured band at 420 and 445 nm. A fitting of the composite spectrums of 14+ and 34+ perfectly recreates the observed final spectrum in Fig. 8 with a mixture of 21% 14+ and 79% 34+, supporting a photochemical process involving both demethylation and demethoxylation. An NMR scale experiment reveals complete loss of the methoxy peak at 4.70 ppm and the appearance of a methanol peak at 3.25 ppm. If the experiment is conducted in air, irradiation leads to 100% conversion of 24+ to 34+, as determined by both NMR and ESI-mass spectrometry.

![Fig. 7](image1.png) Changes in the absorption spectra of complex [2][PF6]4 upon visible light irradiation for various times under anaerobic conditions in acetonitrile with 0.25 M TEA and subsequently, after air oxidation.

![Fig. 8](image2.png) Changes in the absorption spectra of complex [2][PF6]4 (25 μM) upon visible light irradiation under anaerobic conditions in acetonitrile without added TEA and subsequently, after air oxidation.
This photoactivity was surprising as the 1\(^{+}\), and 3\(^{+}\), complexes are stable to irradiation in air or under N\(_2\). However, we had noted that structurally similar ligands can have surprisingly different sensitivities in a previous study of the ruthenium complexes tatp and benzodipyrido[3,2-\(c\)]phenazine. Irradiation of the latter complex in the presence of O\(_2\) yields the quinone, dipyrdo[3,2-\(a\):2',3'-\(c\)]benzo[3,4]phenazine-11,16-quinone, whereas the tatp complex is not changed.

Conclusion

Substitution of the central hydrogens in tatpp for methoxy groups in tatpOMe gives a new electron-rich bridging ligand which was expected to have multi-electron storage capacity like that of tatpp. The electrochemical and optical properties of the free ligand, its Zn(II)-adducts, or its dinuclear ruthenium complex of tatpp. The electrochemical and optical properties of the free ligand, its Zn(II)-adducts, or its dinuclear ruthenium complex of tatpp were expected to have multi-electron storage capacity like that on reduction or oxidation. The methoxy groups are shown to raise the energy of the HOMO and LUMO relative to tatpp but the greater effect is on the HOMO. Due to the high reactivity of tatpOMe towards demethylation and demethoxylation upon reduction or oxidation, the photochemistry of 2\(^{+}\) is not suitable for multi-electron-storage or transfer.

Acknowledgements

The authors wish to thank Professor Peter Kroll and Kenneth Abayan for assistance with the electronic structure calculations. We also want to thank the US National Science Foundation (Grants CHE-0911720 (FMM and NT) and CHE-0840509 (500 MHz NMR)) and the Robert A. Welch Foundation (FMM, Y-1301) for financial support.

References