Redox Control of Conformation and Luminescence of a Dinuclear Ruthenium(II) Complex with a Bis-dipyridophenazine Bridging Ligand

Mara Staffilani,[a] Peter Belser,*[b] Luisa De Cola,[a] and František Hartl*[a]

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This spectroelectrochemical study deals with an interesting luminescent dinuclear complex $[\{Ru(bpy)_2\}_2(\mu\text{-bdppz})]^{4+}$ ($\mathbf{1}^{4+}$), where bpy stands for 2,2′-bipyridine and bdppz for 1,1′-dipyrido[3,2-*a*:2′,3′-*c*]phenazin-1,1′-yldipyrido[3,2-*a*:2′,3′-*c*]phenazine. The electronic coupling between the phenazine moieties through the central C–C bond can be easily modified as a function of the ligand oxidation state. Upon stepwise one-electron reduction in acetonitrile, complex $\mathbf{1}^{4+}$ is reversibly transformed into $\mathbf{1}^{3+}$ and $\mathbf{1}^{2+}$, with consequent major structural and electronic changes of the bridging ligand and with quenched MLCT emission of the excited $Ru(bpy)_2$ moieties.

Introduction

The control of the electronic interaction between different molecular components opens new strategies for the construction of nanometre-sized molecular devices, for example in the field of information and data storage.[1] The possibility to modulate the physical response of chromophoric units by an external stimulus such as redox- or light-driven reaction is a fascinating and booming research topic.[2] An important issue for experimental and theoretical investigations in coordination chemistry in this area is tuneable electronic communication between remote redox-active metal centres with attached chromophoric units or other functionalities (e.g. sensors). The key position of the connecting wire in such an assembly of molecular components can be occupied by a well-defined di- or oligonucleating ligand with tuneable energies of its frontier orbitals and molecular structure as a function of its oxidation state.[3] In this work we focus on an interesting dinucleating α-diimine ligand 1,1′-dipyrido[3,2-*a*:2′,3′-*c*]phenazin-1,1′-yldipyrido[3,2-*a*:2′,3′-*c*]phenazine (bdppz) and its homodinuclear complex $[\{Ru(bpy)_2\}_2(\mu\text{-bdppz})]^{4+}$ ($\mathbf{1}^{4+}$; bpy = 2,2′-bipyridine).[4,5] The bridging ligand consists of two well-known 1,1′-dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz)[4c,6] moieties linked by a C−C bond (see Scheme 1). It is noteworthy that the central part of the bdppz ligand, reaching up to the phenazine nitrogens, formally corresponds to the bridging 3,3′,4,4′-tetraimino-3,3′,4,4′-tetrahydrobiphenyl (tib) ligand with interesting conformation, electronic and redox properties studied in its homodinuclear complex $[\{Ru(bpy)_2\}_2(\mu\text{-tib})]^{4+}$.[7] Comparison between the bdppz and tib ligands will follow.

Results and Discussion

The cyclic and differential pulse voltammograms of $\mathbf{1}^{4+}$ in butyronitrile (Figure 1) reveal a two-electron anodic process (Table 1) that corresponds to unresolved one-electron oxidations of both Ru^{II} centres to Ru^{III} in $\mathbf{1}^{6+}$. The inefficient electronic communication between the two remote Ru centres through the bridging ligand in $\mathbf{1}^{4+}$ is caused to some extent by a large twist at the central C−C bond, in analogy with the related but less extended tib quinonediimine system, that better conjugates the chromophores;[7] the poor overlap between the $d_\pi(Ru)$ orbitals and the central phenazine π-system is also important in this regard.[8,9] The initial reduction of $\mathbf{1}^{4+}$ is indeed largely localised on the phenazine nitrogens of the C−C-linked dppz moieties and occurs as two separate reversible one-electron steps (Table 1). The 2,2′-bipyridine ligands remain insensitive to the reduction of the bridge and reduce reversibly pair-wise in unresolved two-electron processes (Table 1). These assignments have received unambiguous support from the redox properties of the reference[8b] mononuclear complex $[Ru(bpy)_2(dppz)]^{2+}$ ($\mathbf{2}^{2+}$) (Scheme 1 and Table 1) and related diruthenium systems.[9] The pair-wise response of the 2,2′-bipyridine ligands to the reduction indicates the persistent inefficient electronic interaction between the ruthenium centres across the presumably planar two-electron reduced bdppz bridge, in contrast to the tib ligand.[7]

The absorption properties of the dinuclear complex $\mathbf{1}^{4+}$ undergo major changes upon stepwise reduction to $\mathbf{1}^{2+}$ in

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[a] Institute of Molecular Chemistry, Universiteit van Amsterdam,
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands
E-mail: hartl@anorg.chem.uva.nl
[b] Institute of Inorganic and Analytical Chemistry, University of Fribourg, Pérolles, 1700 Fribourg, Switzerland
E-mail: peter.belser@unifr.ch

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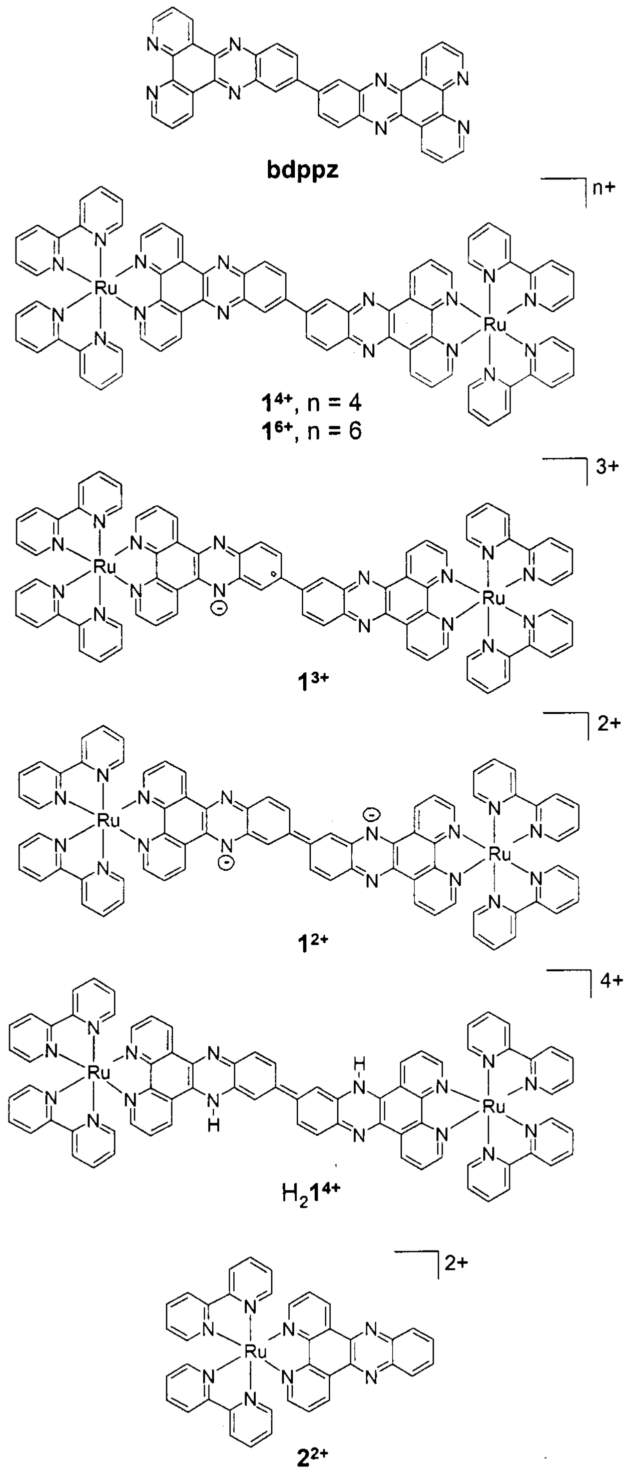


Scheme 1

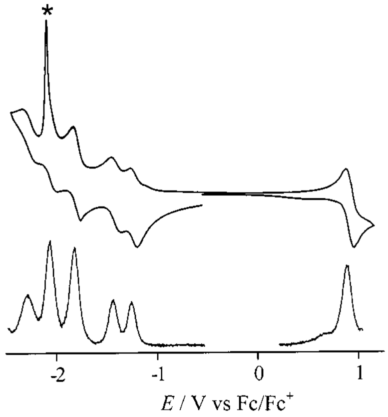


Figure 1. Cyclic voltammogram (top; v = 100 mV s^{-1}) and differential pulse voltammogram (bottom) of 5·10^{-4} M 1^{4+} recorded at a Pt disk electrode in butyronitrile/10^{-1} M Bu_4NPF_6 at 293 K; the asterisk indicates an overlapping adsorption peak

Table 1. Electrochemical data[a] for dinuclear 1^{4+} and mononuclear 2^{2+}

Complex	bpy$^{-1/0}$	bdppz$^{-2/-1}$	bdppz$^{-1/0}$	dppz$^{-1/0}$	Ru$^{II/III}$
1^{4+}	−1.80 (2) −2.04 (2)	−1.42 (1)	−1.23 (1)		+0.91 (2)
2^{2+}	−1.80 (1) −2.06 (1)			−1.39 (1)	+0.94(1)
2^{2+} [b]	−1.73 (1) −1.93 (1)			−1.23 (1)[c]	+0.95(1)

[a] Electrode potentials ($E_{1/2}$, V vs. Fc/Fc$^+$), with the number of transferred electrons in brackets. Experimental conditions: Pt disk working electrode, scan rate 100 mV/s, butyronitrile/10^{-1} M Bu_4NPF_6, 293 K. [b] Experiment in the presence of 1 equivalent of CF_3SO_3H. [c] Cathodic process followed by protonation; reverse oxidation of H2^{2+} occurs at $E_{p,a}$ = −0.29 V.

a UV/Vis spectroelectrochemical cell[10] (Figure 2). The absorption band of 1^{4+} at 407 nm belongs to an intraligand (IL) π-π* transition localised on the phenazine moieties of the bdppz ligand. This band is indeed present in the absorption spectrum of the bdppz ligand, at 413 nm in dichloromethane (insert to Figure 2); it disappears from the absorption spectrum of 1^{4+} upon reduction to 1^{3+} (Figure 2). The pronounced shoulder at 454 nm in the absorption spectrum of 1^{4+} is assigned to a set of metal-to-ligand [d$_\pi$(Ru)-to-π*(bpy)] charge transfer (MLCT) transitions, consistent with the assignments reported for 2^{2+} [4c] and related diruthenium complexes.[9] The shoulder indeed disappears upon the 2e-oxidation of the ruthenium ions to Ru^{III} in 1^{6+} (Scheme 1)[11] but remains almost unchanged upon reduc-

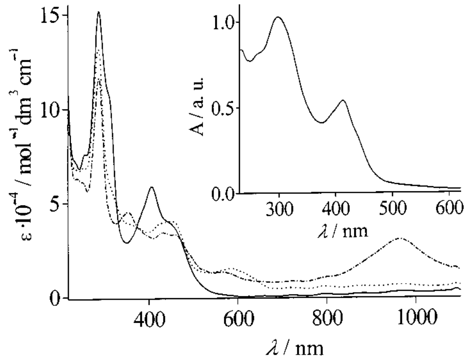


Figure 2. UV/Vis spectra of 5·10^{-4} M 1^{4+} (——), 1^{3+} (– – –) and 1^{2+} (–·–·–) in butyronitrile/3·10^{-1} M Bu_4NPF_6, recorded in an OTTLE cell;[10] inset: UV/Vis spectrum of the noncoordinated bdppz ligand (saturated solution in dichloromethane)

tion of $\mathbf{1}^{4+}$ to $\mathbf{1}^{3+}$ (Figure 2). A new structured absorption band of 1e-reduced $\mathbf{1}^{3+}$ at ca 580 nm belongs to IL transitions due to the radical [bdppz]$^{\cdot-}$ ligand (Figure 2), similarly to that reported for $\mathbf{2}^{2+}$.[8b] Importantly, when proceeding further with the reduction to $\mathbf{1}^{2+}$, a new broad and intense low-lying absorption band arises at 965 nm (Figure 2). It corresponds to an IL π-π* transition within the new π-system of the planar C=C-linked phenazine moieties of [bdppz]$^{2-}$. This absorption band shifts to 650 nm in the UV/Vis spectrum of the complex $H_2\mathbf{1}^{4+}$ (Figure 3 and Scheme 1) formed by protonation of the negatively charged phenazine nitrogens in $\mathbf{1}^{2+}$ (see Exp. Sect.). It is noteworthy that $H_2\mathbf{1}^{4+}$ deprotonates smoothly back to orange $\mathbf{1}^{4+}$ upon addition of H_2O_2.

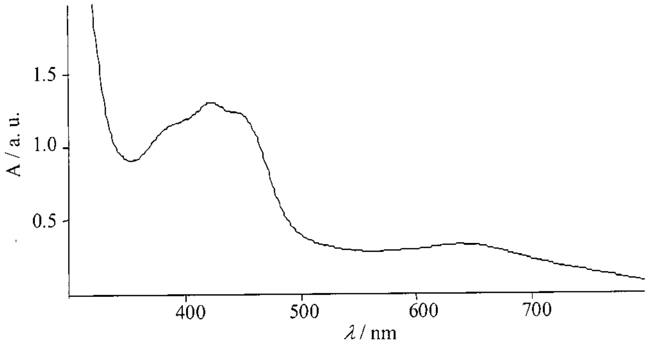


Figure 3. UV/Vis spectrum of $H_2\mathbf{1}^{4+}$ produced by chemical reduction of $\mathbf{1}^{4+}$ with Zn in deaerated acidified acetonitrile

The chemical reversibility of the coupled reduction/protonation processes and their localisation on the phenazine moieties was also revealed by cyclic voltammetry. For reference $\mathbf{2}^{2+}$, the phenazine-centred reduction at the dppz ligand in acetonitrile becomes electrochemically irreversible in the presence of exactly one equivalent of trifluoromethanesulfonic acid. The cyclic voltammogram indeed exhibits a large separation between the reduction of $\mathbf{2}^{2+}$, at $E_{p,c} = -1.23$ V, and the reverse anodic process, at $E_{p,a} = -0.29$ V, assigned to the oxidation of $H\mathbf{2}^{2+}$. In contrast, the bpy-centred cathodic steps are much less affected by the protonation, only being shifted by ca. 100 mV to more positive potentials, while the ruthenium-centred oxidation remains unchanged (Table 1). The product $H\mathbf{2}^{2+}$ does not decompose during the complete cyclic voltammetric scan (v = 100 mV/s), as testified by identical $i_{p,c}$ (reduction of $\mathbf{2}^{2+}$) and $i_{p,a}$ (oxidation of $H\mathbf{2}^{2+}$) peak current values. An analogous voltammetric response was also observed for dinuclear $\mathbf{1}^{4+}$ in acidified acetonitrile; however, the voltammetric peaks associated with the electrochemical reduction and coupled protonation of the phenazine nitrogen sites become very broad and determination of the cathodic and anodic peak potentials lacks precision.

The emission of complex $\mathbf{1}^{4+}$ at 650 nm with lifetime τ = 130 ns in acetonitrile (Figure 4) becomes completely quenched upon the stepwise electrochemical reduction to $\mathbf{1}^{3+}$ and $\mathbf{1}^{2+}$. The same result was obtained for reference $\mathbf{2}^{2+}$ and 1e-reduced $\mathbf{2}^{+}$. The corresponding experiments were conveniently run in situ within the thin-layer spectroelectrochemical cell, as described in the Exp. Sect. The luminescence can be switched OFF and ON repeatedly between $\mathbf{1}^{3+}$ and $\mathbf{1}^{4+}$, respectively. For $\mathbf{1}^{3+}$ (and $\mathbf{2}^{+}$) the quenching is attributed to efficient electron transfer from the electrochemically reduced phenazine moiety of bdppz (or dppz, in the case of $\mathbf{2}^{+}$) to the excited *{Ru^{III}(bpy$^{\cdot-}$)} unit. The value of the Gibbs energy change associated with the electron transfer process can be estimated through the zero-zero excitation energy E_{00} and the electrochemical potentials of the ground-state redox couples [Equation (1), for $\mathbf{1}^{3+}$], where $E°(\text{bpy}^{-1/0})$ denotes the 1e-reduction of the $Ru(bpy)_2$ moiety.

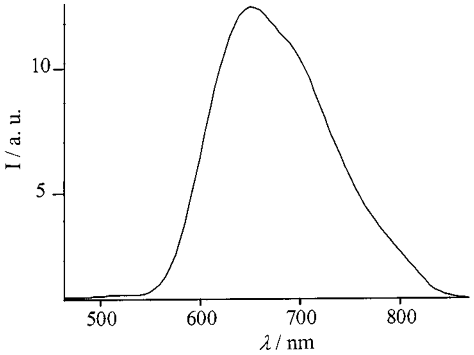


Figure 4. Emission of $\mathbf{1}^{4+}$ in acetonitrile, recorded upon excitation with 450 nm light

$$\Delta G° = E°(\text{bdppz}^{-1/0}) - E°(\text{bpy}^{-1/0}) - E_{00} = -1.23 - (-1.80) - 2.14\ \text{eV} < 0 \quad (1)$$

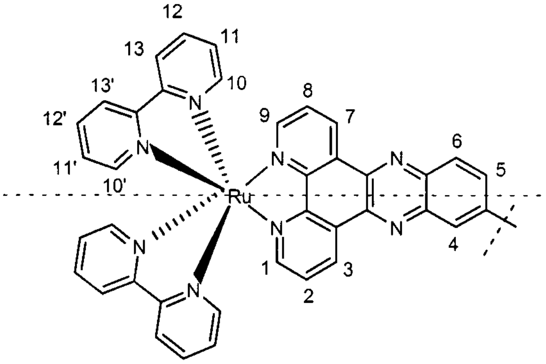
No luminescence was observed for 2e-reduced $\mathbf{1}^{2+}$ or its protonated form $H_2\mathbf{1}^{4+}$ (see Exp. Sect.), probably due to its low-lying non-luminescent bdppz-centred π-π* excited state (see above).

In conclusion, we present the redox behaviour of a diruthenium complex where the phenazine portion of the bridging bdppz ligand can be reversibly reduced in two separate one-electron steps. Interestingly, in the two-electron reduced state the bdppz ligand becomes planar. Its central C−C-linked bis(phenazine) portion responds to the reductions similarly to the less extended bis(*o*-quinonediimine) tib ligand.[7] In the planar conformation the bridging [bdppz]$^{2-}$ ligand is characterized by a new low-lying excited state, localised on the planar C=C-linked bis(phenazine) portion, that acts as an energy trap for the higher-lying (MLCT) excited states. Importantly, the energy of the lowest excited state can be increased upon reversible protonation. These properties of the binucleating bdppz ligand classify it as a redox- and pH-controllable molecular switch of long-distance electron/energy transfer in appropriately selected donor-acceptor dyads. In this regard, detailed photophysical and spectroelectrochemical investigations of bdppz-bridged homo- and heterodinuclear complexes are in progress.

Experimental Section

General: All solvents and reagents used in the preparations were reagent grade, purchased from Fluka or Aldrich, and used as supplied. Silica gel preparative plates and aluminium oxide chromatographic columns were used for purification of the metal complexes. The preparative SiO_2 plates were made of silica gel purchased from Merck (60, particle size 0.040−0.063 mm) and prepared according to the procedure indicated by Merck. Aluminium oxide for chromatography was purchased from Fluka (type 507 C neutral, Brockmann grade I, particle size 0.05−0.15 mm, pH 7.0 ± 0.5). For electrochemistry, butyronitrile (Acros) was dried over CaH_2 and freshly distilled under nitrogen prior to use; acetonitrile (Fluka, spectroscopic grade) was used as received. The supporting electrolyte Bu_4NPF_6 (Aldrich) was recrystallized twice from ethanol and dried overnight under reduced pressure at 60 °C.

^1H NMR spectra were recorded on a Varian Gemini 300 (300.075 MHz) spectrometer; chemical shifts are given in ppm, using the solvent itself as internal standard. Assignment of the signals was performed using the COSY technique. The numbering of the protons is shown in Scheme 2. ESI (Electron Spray Ionisation) mass spectra were obtained with a Bruker FTMS 4.7 T Bio APEXII spectrometer. UV/Vis absorption spectra were recorded on a Hewlett Packard 8453 diode-array spectrophotometer, and the reported emission spectrum (corrected for the photomultiplier response) on a Spex 1681 spectrophotometer (λ_{exc} = 450 nm).



Scheme 2

Cyclic voltammetric and differential pulse voltammetric scans were performed with a gas-tight single-compartment cell under an atmosphere of dry nitrogen or argon. The cell was equipped with a Pt disk working (apparent surface area of 0.42 mm^2), Pt wire auxiliary, and Ag wire pseudoreference electrodes. The working electrode was carefully polished with a 0.25 μm-grain diamond paste between scans. All redox potentials are reported against the ferrocene-ferrocenium (Fc/Fc$^+$) redox couple used as an internal standard[12] ($E_{1/2}$ = 0.42 V vs. SCE in acetonitrile). The potential control was achieved with a PAR Model 283 potentiostat. UV/Vis spectroelectrochemical experiments were performed with an optically transparent thin-layer electrochemical (OTTLE) cell,[10] equipped with a Pt minigrid working electrode and quartz optical windows. The controlled-potential electrolyses were carried out with a PA4 potentiostat (EKOM, Czech Republic). All electrochemical samples were $5\cdot10^{-4}$ M in the studied complex and contained $3\cdot10^{-1}$ M Bu_4NPF_6. The spectroelectrochemical cell was also conveniently employed for recording emission spectra during the electrochemical quenching experiments and determination of emission lifetime. In this case the emission spectra were recorded using an optical fibre connected to a nitrogen laser and a streak camera (Hamamatsu C5680−21), equipped with a M 5677 sweep unit. Excitation at 337 nm was achieved by a pulsed (fwhm 600 ps) nitrogen laser (LTB, MGS 405 TD) operating at a repetition rate of 20 Hz.

1,1′-Dipyrido[3,2-*a*:2′,3′-*c*]phenazin-1,1′-yldipyrido[3,2-*a*:2′,3′-*c*]-phenazine (bdppz): 1,10-phenanthroline-5,6-dione[4] (0.420 g, 2.0 mmol) and 3,3′,4.4′-biphenyltetramine (0.214 g, 1.0 mmol) were suspended in 10 mL acetic acid (100%) and heated at 120 °C for 1 h. After cooling to room temperature, 100 mL of water was added to the reaction mixture. The olive-green precipitate was filtered off, washed with water, aqueous sodium hydrogen carbonate (10%) and again with water. The solid was dried under vacuum at 50 °C (0.484 g, yield 86%). The bdppz ligand is practically insoluble in all common solvents, therefore a direct analytical proof has not been possible.

[{Ru(bpy)$_2$}$_2$(μ-bdppz)](PF$_6$)$_4$ (1^{4+}): $[Ru(bpy)_2Cl_2]\cdot2H_2O$ (0.104 g, 0.2 mmol),[5] bdppz (0.056 g, 0.1 mmol) and 2 drops of HPF_6 (60% solution in water) were suspended in ethylene glycol (6 mL) and heated in a microwave oven (3 times for 2 min). The solvent was removed under reduced pressure. Water (20 mL) and NH_4PF_6 (1 g) were then added to produce a red precipitate that was separated by suction filtration. The crude product was purified on a column of neutral aluminium oxide (10 × 2 cm) with acetone/water (98:2) as eluent. The orange-red band (TLC: R_f = 0.22, support SiO_2, eluent $MeCN/H_2O/MeOH/KNO_3$ 4:1:1:0.1) was collected, the solvents were removed under reduced pressure and the residual solid was further purified on SiO_2 plates ($MeCN/H_2O$/*tert*-butyl alcohol/KNO_3 4:1:1:0.1). Isolation (with acetone/NH_4PF_6 as eluent) of the orange-red band gave the pure product (0.055 g, 28% yield). ^1H NMR (CD_3CN): bdppz signals δ = 7.92 (dd, 4 H, H2 and H8), 8.20 (d, 4 H, H1 and H9), 8.69 (d, 2 H, H6), 8.76 (d, 2 H, H5), 9.04 (s, 2 H, H4), 9.71 (d, 4 H, H3 and H7); bpy signals δ = 7.28 (dd, 2 H, H11), 7.47 (dd, 4 H, H11′), 7.75 (d, 4 H, H10), 7.86 (d, 4 H, H10′), 8.03 (dd, 4 H, H12), 8.12 (dd, 4 H, H12′), 8.53 (d, 4 H, H13), 8.56 (d, 4 H, H13′). See Scheme 2 for proton numbering. ESI-MS: *m*/*z* = 839.59 [$M^+ - 2PF_6^-$], 551.74 [$M^+ - 3PF_6^-$], 347.56 [$M^+ - 4PF_6^-$]. HRMS for $C_{76}H_{50}N_{16}Ru_2$ (1389.5): calcd. 347.5617; found 347.5618.

Reversible Protonation of 2e-Reduced 1^{2+}: The doubly protonated complex H_2**1**$^{4+}$ was prepared in situ by reducing **1**$^{4+}$ with metallic zinc in acidified acetonitrile or acetone. The parent complex (4.6 mg, $2.3\cdot10^{-3}$ mmol) was dissolved in 50 mL of the solvent. This solution (8 mL) was acidified with HCl (2 mL) and stirred with added Zn granules (1 g, about 1 mm size) for 15 min. The UV/Vis spectrum of the product (see Figure 3) was identical with that of H_2**1**$^{4+}$ generated in situ by reducing **1**$^{4+}$ in acetonitrile in the UV/Vis spectroelectrochemical cell in the presence of exactly two equivalents of trifluoromethanesulfonic acid. Addition of hydrogen peroxide to the green solution of H_2**1**$^{4+}$ resulted in a rapid and complete recovery of orange **1**$^{4+}$, as confirmed by UV/Vis spectroscopy.

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