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Chapter 6

(Spectro)electrochemical and Photophysical Study of Homodinuclear Ruthenium(II) and Osmium(II) Complexes with Bridging Bis-(dipyridophenazine) Ligand.

The (spectro)electrochemical and photophysical properties of \( [(bpy)_2Ru(bidppz)Ru(bpy)_2]^4^+ \), \( [(bpy)_2Os(bidppz)Os(bpy)_2]^4^+ \) and the bridging ligand bidppz (bpy = 2,2'-bipyridine, bidppz = 1,1'-dipyrido[3,2-a:2',3'-c]phenazin-1,1'-yldipyrido[3,2-a:2',3'-c]phenazine) are investigated. Time-resolved spectroscopic studies were performed on (sub)pico- to microsecond time scales, offering insight into the excited states responsible for the solvent-dependent photophysical behavior of the two complexes. In particular, \( [(bpy)_2Ru(bidppz)Ru(bpy)_2]^4^+ \) shows long excited state lifetime, 9.7 \( \mu \)s, in deaerated dichloromethane solution, that becomes much shorter (360 ns) in deaerated butyronitrile. The solvent plays a crucial role for the spectroscopic properties of this complex, since the energy of the triplet metal-to-ligand charge-transfer (\( ^3\)MLCT) state is influenced by the polarity of the medium. (Sub)pico-second transient absorption spectra in dichloromethane indicate thermal population of the long-lived triplet intraligand (\( ^3\)IL) state of the bridging ligand from the higher lying \( ^3\)MLCT state. For \( [(bpy)_2Os(bidppz)Os(bpy)_2]^4^+ \) in dichloromethane the \( ^3\)MLCT state lies low in energy and no interaction of this state with the \( ^3\)IL state of the bridging ligand is observed.
6.1 Introduction

One of the strategies employed to elongate the excited-state lifetime of ruthenium polypyridyl complexes has been the use of flat aromatic ligands as appended moieties or as part of the chelating unit coordinated to the metal ion. In some conditions, they are indeed able to induce an equilibrium between their long lived triplet intraligand (\(^3\)IL) excited state and the triplet metal-to-ligand charge transfer (\(^3\)MLCT) excited state of the ruthenium unit, resulting in a longer \(^3\)MLCT emission decay time.\(^{1-3}\)

![Diagram of Ru-bidppz](image)

\[\text{M-bidppz-M}^{2+}\]

\[\text{Ru-bidppz}^{2+}\]

\[\text{Os-bidppz}^{2+}\]

\[\text{Ru-bidppz-Ru}\]

\[\text{Os-bidppz-Os}\]

Scheme 6.1. Schematic representation of the investigated compounds and the reference complex [Ru-dppz]\(^{2+}\).

In this regard, among the most investigated systems are the ruthenium polypyridyl complexes containing either a pyrene\(^{2,3}\) or a dppz (dppz = dipyrido[3,2-a:2',3'-c]phenazine)\(^{4-11}\) unit (see also Section 1.5). In particular, ruthenium dppz complexes have stimulated a lot of research due to their "light switch" behavior in aqueous solution in the presence of DNA.\(^{4-6,11}\) The photophysical properties of dppz metal complexes\(^{6,8,9,11,12}\) are
Homodinuclear Ruthenium(II) and Osmium(II) Bis-DPPZ Complexes

rather intriguing, as well as those of several similar systems containing pyrido-phenazine unit as part of the bridging ligand.\textsuperscript{13-18} The presence of an electron withdrawing group, such as the phenazine moiety, and the weak electronic interaction between this unit and the phenanthroline chelating site have attracted a lot of attention.

In our study a bridging ligand (1,1'-dipyrido[3,2-a:2',3'-c]phenazine-1,1'-yl)dipyrido[3,2-a:2',3'-c]phenazine, bidppz\textsuperscript{19,20} consisting of two dppz moieties linked by a single C-C bond has been employed to construct two luminescent dinuclear homometallic systems containing ruthenium or osmium units. The two metal units bind ancillary 2,2'-bipyridine ligands. The homometallic complexes are indicated hereinafter as [Ru-bidppz-Ru]\textsuperscript{4+} and [Os-bidppz-Os]\textsuperscript{4+} (Scheme 6.1).

In this Chapter the (spectro)electrochemical and the photophysical properties of the two complexes are presented. The mononuclear [Ru-dppz]\textsuperscript{2+} complex (Scheme 6.1) is also discussed as the reference compound. By time-resolved spectroscopic investigations performed in a wide time-resolution range (from (sub)pico- to microseconds) and in different solvents, insight into the excited states responsible for the spectroscopic behavior of the two complexes is obtained.

Furthermore, the spectroscopic properties and switching behavior of the electrochemically two-electron reduced ruthenium dinuclear complex are presented.

6.2 Results and Discussion.

6.2.1 Redox properties.

The electrochemical data for the complexes [Ru-bidppz-Ru]\textsuperscript{4+} and [Os-bidppz-Os]\textsuperscript{4+}, and the reference compounds [Ru-dppz]\textsuperscript{2+}, [Ru(bpy)]\textsuperscript{2+} and Os[(bpy)$_3$]\textsuperscript{2+}, are summarized in Table 6.1. The cyclic and differential pulse voltammograms (CV and DPV) for [Ru-bidppz-Ru]\textsuperscript{4+} are reported in Figure 6.1.

The voltammograms of [Ru-bidppz-Ru]\textsuperscript{4+} and [Os-bidppz-Os]\textsuperscript{4+} are consistent with metal(II)-based oxidations and several ligand-based reductions.

In the cathodic region, the first two steps occur at \(-1.23\) and \(-1.42\) V for [Ru-bidppz-Ru]\textsuperscript{4+}, and at \(-1.22\) and \(-1.41\) V for [Os-bidppz-Os]\textsuperscript{4+}. On the basis of the integrated DPV current intensities they are consistent with two one-electron reduction processes (see Figure 6.1 for [Ru-bidppz-Ru]\textsuperscript{4+}). These redox potentials are close to that of [Ru-dppz]\textsuperscript{2+}, \(-1.39\) V (Table 6.1), where the first reduction occurs at the phenazine part of the dppz ligand.\textsuperscript{9,21} Thus, the first two steps in [Ru-bidppz-Ru]\textsuperscript{4+} and [Os-bidppz-Os]\textsuperscript{4+} are assigned to the consecutive reduction of the two phenazine moieties of the bridging ligand. For the dppz\textsuperscript{10,21} and dppz-based ligands, such as tpphz (tpphz = tetrapyrido[3,2-a:2',3'-c:3"-h:2'':3":"-j]phenazine),\textsuperscript{18} the lowest unoccupied molecular orbital (LUMO) is mainly localized on the phenazine part of
Chapter 6

the ligand, with negligible contribution by the two coordinating nitrogen atoms of their phenantroline part. By analogy, we can expect a similar situation for bidppz, in agreement with the electrochemical data. Furthermore, in [Ru-bidppz-Ru]^{4+} and [Os-bidppz-Os]^{4+} a poor electronic communication exists between the coordinated metal ions and the phenazine units, explaining the negligible effect of the nature of the metal ion on the first two reduction potentials. By contrast, the separation of the two cathodic waves of the bridging ligand points to a strong electronic communication between the two phenazine moieties.

Table 6.1. Electrochemical data of the investigated complexes and reference compounds$^a$

<table>
<thead>
<tr>
<th>Complex</th>
<th>bidppz$^{2+/0}$</th>
<th>bpy$^{1+/0}$</th>
<th>bidppz$^{2+/0}$</th>
<th>bidppz$^{1+/0}$</th>
<th>dppz$^{1+/0}$</th>
<th>Ru$^{II/III}$</th>
<th>Os$^{II/III}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru-bidppz-Ru]^{4+}</td>
<td>-2.26 (1)</td>
<td>-1.80 (2)</td>
<td>-1.42 (1)</td>
<td>-1.23 (1)</td>
<td></td>
<td>+0.91 (2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-2.04 (2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Os-bidppz-Os]^{4+}</td>
<td>-2.23 (1)</td>
<td>-1.74 (2)</td>
<td>-1.41 (1)</td>
<td>-1.22 (1)</td>
<td></td>
<td>+0.47 (2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-2.03 (2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru-dppz]$^{2+}$</td>
<td>-1.80 (1)</td>
<td></td>
<td>-1.39 (1)</td>
<td>+0.94 (1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-2.06 (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru-dppz]$^{2+/b}$</td>
<td>-1.73 (1)</td>
<td></td>
<td>-1.23 (1)$^c$</td>
<td>+0.95 (1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(irrev)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1.93 (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(bpy)$_3$]$^{2+}$</td>
<td>-1.72 (1)</td>
<td></td>
<td></td>
<td>+0.89 (1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-1.93 (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Os(bpy)$_3$]$^{2+}$</td>
<td>-1.59 (1)</td>
<td></td>
<td></td>
<td>+0.45 (1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-1.77 (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Redox potentials ($E_{1/2}$) in Volt vs Fe/Fe$^+$, in butyronitrile at 293 K. In brackets, the number of transferred electrons. $^b$Experiment in the presence of one equivalent of CF$_3$SO$_3$H. $^c$Cathodic process coupled to protonation, $\Delta E_p = 1.46$ V for the chemically reversible process.

The third and fourth steps of [Ru-bidppz-Ru]^{4+} (−1.80 and −2.04 V) and [Os-bidppz-Os]^{4+} (−1.74 and −2.03 V) occur as two bielectronic cathodic waves assigned to two pairwise one-electron reductions of the bipyridine ligands at the remote metal centers. They are shifted to

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more negative potentials than the first two reductions of the bpy ligands in $[\text{Ru(bpy)}_3]^{2+}$ (-1.72 and -1.93 V) and $[\text{Os(bpy)}_3]^{2+}$ (-1.59 and -1.77 V), respectively, as a result of the coulombic repulsion due to the electron density on the primary reduced bridging ligand, bidppz$^{2-}$. The pair-wise response of the ancillary bipyridine ligands to the reduction indicates an inefficient electronic interaction between the ruthenium centers across the presumably planar two-electron reduced bidppz$^{2-}$ bridging ligand (see Scheme 6.1).

A fifth step is observed for $[\text{Ru-bidppz-Ru}]^{4+}$ and $[\text{Os-bidppz-Os}]^{4+}$ as one-electron wave at -2.26 and -2.23 V, respectively, ca. 1.0 V more negatively than the first bidppz-localized reduction in the two dinuclear complexes. Similar potential difference has been reported for the first and second reductions of the dppz ligand in $[\text{Ru-dppz}]^{2+}$. By analogy, the fifth step is then assigned to the further reduction of the bridging ligand to bidppz$^{3-}$.

In the anodic region, $[\text{Ru-bidppz-Ru}]^{4+}$ and $[\text{Os-bidppz-Os}]^{4+}$ are oxidized at +0.91 and +0.47 V, respectively, in an unresolved doubly one-electron process, which once again reveals a weak electronic communication between the two metals. Similar potential difference is commonly observed for other osmium complexes and their isostructural ruthenium ones, consistent with the higher energy of the 5d-osmium orbitals.

**Figure 6.1** Cyclic voltammogram (top; $v = 100$ mV s$^{-1}$) and differential pulse voltammogram (bottom) of $5 \times 10^{-4}$ M $[\text{Ru-bidppz-Ru}]^{4+}$, recorded at a Pt disk electrode in butyronitrile/10$^{-1}$ M Bu$_4$NPF$_6$ at 293 K. The asterisk indicates an overlapping adsorption peak.

6.2.2 UV-Vis steady-state absorption.

UV-Vis absorption spectra were recorded for the investigated complexes $[\text{Ru-bidppz-Ru}]^{4+}$ and $[\text{Os-bidppz-Os}]^{4+}$ and, for easier assignments, for the uncoordinated bidppz ligand in dichloromethane, Figure 6.2. Changing the solvent to acetonitrile causes only minor
changes. The UV-Vis absorption data are summarized in Table 6.2. Due to the poor solubility in all common solvents, the absorption molar coefficients of ligand bidppz could not be determined with precision.

![UV-Vis spectra](image)

**Figure 6.2** UV/Vis spectra of [Ru-bidppz-Ru]$^{4+}$ (----), [Os-bidppz-Os]$^{4+}$ (----) and bidppz (........) in CH$_2$Cl$_2$. Inset: room temperature emission spectra of [Ru-bidppz-Ru]$^{4+}$ (----) and [Os-bidppz-Os]$^{4+}$ (----) ($\lambda_{exc} = 460$ nm), and 77 K phosphorescence of bidppz (........) in MeOH/EtOH matrix containing ZnCl$_2$ ($\lambda_{exc} = 460$ nm).

The UV/Vis absorption spectra of [Ru-bidppz-Ru]$^{4+}$ and [Os-bidppz-Os]$^{4+}$ show similar features (Figure 6.2). In the UV region, the band at 290 nm and the shoulder at 300 nm are assigned to singlet intraligand (1IL) $\pi-\pi^*$ transitions of the ancillary bipyridines and the bidppz ligand, respectively. The band at 410 nm, also present in the absorption spectrum of bidppz (Figure 6.2), is referred to a $^1$IL $\pi-\pi^*$ transition localized on the phenazine moiety. In the region 440-540 nm, the electronic absorption spectra of the dinuclear metal complexes [Ru-bidppz-Ru]$^{4+}$ and [Os-bidppz-Os]$^{4+}$ show absorptions assigned to singlet metal-to-ligand charge transfer (1MLCT) transitions from the d$_e$ orbitals of the metal to the $\pi^*$ orbitals of the ancillary bipyridines and the bridging bidppz ligand. Absorption due to 1MLCT transitions from d$_e$ orbitals of the metal to the $\pi^*$ system of the phenazine part of bidppz is expected to lie at lowest energy, on the grounds of the electrochemical data. However, due to the poor overlap of the d$_e$ orbitals and the $\pi^*$ system of the central phenazine part, the oscillator strength for this transition is too small to permit observation of the corresponding absorption band. As expected, MLCT absorption bands of [Os-bidppz-Os]$^{4+}$ are red-shifted compared to the ruthenium complex. [Os-bidppz-Os]$^{4+}$ also shows a weak absorption tailing
more to the red (540-680 nm), assigned to spin-forbidden electronic transitions ($^3$MLCT states) that become partially allowed due to the strong spin-orbit coupling in the osmium complexes.

Table 6.2. UV/Vis spectroscopic data of the investigated compounds in CH$_2$Cl$_2$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{\text{abs}}$ / nm ($\varepsilon \times 10^{-4}$ / dm$^3$ mol$^{-1}$cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru-bidppz-Ru]$^{4+}$</td>
<td>289 (13.7), 410 (5.5), 464 (sh, 3.2)</td>
</tr>
<tr>
<td>[Os-bidppz-Os]$^{4+}$</td>
<td>293 (15.9), 410 (5.8), 490 (3.4)</td>
</tr>
<tr>
<td>bidppz</td>
<td>297, 413</td>
</tr>
</tbody>
</table>

The UV-Vis absorption spectra were also recorded for the oxidized ruthenium and osmium dinuclear complexes, [Ru-bidppz-Ru]$^{6+}$ and [Os-bidppz-Os]$^{6+}$ respectively (see Scheme 6.1), and for their one- and two-electron reduced species, [Ru-bidppz-Ru]$^{3+}$ and [Os-bidppz-Os]$^{3+}$ with $n = 3, 2$ (see Scheme 6.1), using an optically-transparent thin-layer electrochemical (OTTLE) cell. The absorption spectra of the ruthenium and osmium redox products are depicted in Figures 6.3 and 6.4, respectively.

The electronic absorption properties of [Ru-bidppz-Ru]$^{4+}$ and [Os-bidppz-Os]$^{4+}$ undergo similar changes upon oxidation and stepwise reduction (Figures 6.3 and 6.4, respectively). The spectra of two-electron oxidized [Ru-bidppz-Ru]$^{6+}$ and [Os-bidppz-Os]$^{6+}$ reveal disappearance of the bands above 410 nm, consistent with their assignment to MLCT transitions and the oxidation of the metal centers, while the intraligand bands in the UV region and at 407 nm become red-shifted. Upon one-electron reduction to [Ru-bidppz-Ru]$^{3+}$ and [Os-bidppz-Os]$^{3+}$ the absorption band at 407 nm disappears, while the shoulder at 454 nm, in the case of the diruthenium complex, and the band at 490 nm, in the case of the diosmium complex, remain almost unchanged. Importantly, a new absorption band was observed at 580 nm, overlapping with the $^3$MLCT absorption band in the case of [Os-bidppz-Os]$^{3+}$. The new band was proven to correspond to an IL $\pi$-$\pi^*$ transition of the phenazine radical anion. Upon the second reduction, [Ru-bidppz-Ru]$^{2+}$ and [Os-bidppz-Os]$^{2+}$ are characterized by decreased intensity of the band at 580 nm and appearance of a new lower-lying band at 965 nm. This band is assigned to an intraligand transition within the presumably planar bidppz$^{2-}$ bridging ligand, most likely at the C=C-linked phenazine moieties.
Figure 6.3 UV/Vis spectra of [Ru-bidppz-Ru]^{4+} (---), [Ru-bidppz-Ru]^{6+} (-----), [Ru-bidppz-Ru]^{3+} (--), and [Ru-bidppz-Ru]^{2+} (- - -) in butyronitrile solution (5 × 10^{-4} M) with Bu_{4}NPF_{6} (3 × 10^{-1} M), recorded within an OTTLE cell.

Figure 6.4 UV/Vis spectra of [Os-bidppz-Os]^{4+} (---), [Os-bidppz-Os]^{6+} (-----), [Os-bidppz-Os]^{3+} (--), and [Os-bidppz-Os]^{2+} (- - -) in butyronitrile solution (5 × 10^{-4} M) with Bu_{4}NPF_{6} (3 × 10^{-1} M), recorded within an OTTLE cell.
6.2.3 Luminescence.

The emission properties of [Ru-bidppz-Ru]^{4+} and [Os-bidppz-Os]^{4+} were investigated at 293 K, in dichloromethane and butyronitrile solutions, and at 77 K, in butyronitrile rigid matrix, upon excitation at 460 nm. The bidppz ligand was investigated at 77 K, in methanol/ethanol 1:4 (v/v) rigid matrix, upon excitation at 350 nm. Inset of Figure 6.2 shows the emission spectra of [Ru-bidppz-Ru]^{4+} and [Os-bidppz-Os]^{4+} in dichloromethane solution at 293 K, and the phosphorescence band of bidppz, at 77 K. The photophysical data are summarized in Table 6.3. Data for the reference compounds [Ru-dppz]^{2+}, [Ru(bpy)_{3}]^{2+} and [Os(bpy)_{3}]^{2+} are also included for comparison.

Table 6.3. Emission data of the investigated complexes and reference compounds.

<table>
<thead>
<tr>
<th>Complex</th>
<th>RT^a in CH_{2}Cl_{2}</th>
<th>in BuCN</th>
<th>77K in BUCN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>\lambda_{em}/ nm</td>
<td>\tau/ ns</td>
<td>\lambda_{em}/ nm</td>
</tr>
<tr>
<td>[Ru-bidppz-Ru]^{4+}</td>
<td>613</td>
<td>9700</td>
<td>675</td>
</tr>
<tr>
<td>[Os-bidppz-Os]^{4+}</td>
<td>750</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>bidppz^{b}</td>
<td></td>
<td></td>
<td>27000^{c}</td>
</tr>
<tr>
<td>[Ru-dppz]^{2+}</td>
<td>600</td>
<td>590</td>
<td>624</td>
</tr>
<tr>
<td>[Ru(bpy)_{3}]^{2+}</td>
<td>600</td>
<td>610</td>
<td>1100^{d}</td>
</tr>
<tr>
<td>[Os(bpy)_{3}]^{2+}</td>
<td>717</td>
<td>733</td>
<td>60^{e}</td>
</tr>
</tbody>
</table>

aDeaerated solutions. bSolutions containing ZnCl_{2}. cData from time-resolved transient absorption measurements in CH_{3}CN. dRef. 16. eRef. 26

The emission maxima of the dinuclear [Ru-bidppz-Ru]^{4+} and [Os-bidppz-Os]^{4+} complexes depend on the solvent polarity (Table 6.3). Solvatochromism is expected for metal complexes with MLCT lowest excited state. However, for [Ru-bidppz-Ru]^{4+} the change in solvent polarity induces a dramatic change in photophysical properties.

The luminescence of the dinuclear compound [Ru-bidppz-Ru]^{4+} in butyronitrile shows a maximum at 675 nm, red shifted compared to the reference complexes [Ru-dppz]^{2+} and [Ru(bpy)_{3}]^{2+} emitting at 624 and 610 nm, respectively (Table 6.3). This proves that the emitting excited state of [Ru-bidppz-Ru]^{4+} has more CT character, with the excited electron localized on a phenazine \pi^{*} orbital, lying at a lower energy than the lowest \pi^{*} orbital of the bpy and dppz ligands. This result is consistent with what has already been deduced from the electrochemical data: the two phenazine moieties of bidppz are electronically coupled and the LUMO of the extended bidppz is low in energy. The lifetime of the emitting excited state of [Ru-bidppz-Ru]^{4+} is 360 ns in deaerated solution (Table 6.3), and drops to 210 ns in air-equilibrated conditions. The emission decay time is of the same order of magnitude as that of the reference complex [Ru-dppz]^{2+} (500 ns in a deaerated solution, Table 6.3), consistent
with an emitting excited state of identical nature \( ^3\text{MLCT} \). In particular, the shorter lifetime of the dinuclear complex is due to the lower energy of the emission, in agreement with the energy gap law. Changing solvent to less polar dichloromethane, the emission maximum of \([\text{Ru-bidppz-Ru}]^{4+}\) shifts to higher energy (613 nm, inset to Figure 6.2) similarly, even though more pronounced, to \([\text{Ru-dppz}]^{2+}\) and \([\text{Ru(bpy)}_3]^2+\), emitting at 600 nm (see Table 6.3). The blue shift is expected for MLCT states with a larger dipole moment in the excited state. Surprisingly, the emission decay time of \([\text{Ru-bidppz-Ru}]^{4+}\) in de aerated dichloromethane solution, is very long, 9.7 \(\mu s\), and significantly exceeds the lifetime of 590 ns determined for the model compound \([\text{Ru-dppz}]^{2+}\) under the same experimental conditions (Table 6.3). The lifetime of \([\text{Ru-bidppz-Ru}]^{4+}\) drops to 800 ns when measured in air-equilibrated solution. The long lifetime of 9.7 \(\mu s\) cannot simply be attributed to the same emitting excited state observed in butyronitrile. The sensitivity towards dioxygen suggests that a triplet ligand-centered state is populated, and is responsible for the long emission lifetime of the complex. In order to determine the energy of the \(^3\text{IL}\) state, the emission properties of the bidppz ligand and its metal Zn(II) complex have been studied. Beside the increased solubility of the ligand, the coordination of bidppz to Zn\(^{2+}\) allows a better comparison of the properties of the ligand with its transition metal complexes, when coordinated to a divalent ion.

The uncoordinated bridging ligand bidppz shows broad fluorescence and phosphorescence bands at 473 and 590 nm, respectively, at 77 K in methanol/ethanol 1:4 (v/v) matrix upon excitation at 350 nm. The emission spectra were also recorded for a solution containing bidppz with a large excess of ZnCl\(_2\). For the Zn-bidppz complex, the fluorescence and phosphorescence bands become structured and shift to 421 and 586 nm, respectively (Table 3, inset to Figure 6.2).

These investigations show that the triplet state of the bidppz coordinated to Zn(II) metal ions lies at low energy (about 17065 cm\(^{-1}\)), very close to the \(^3\text{MLCT}\) excited state (16920 cm\(^{-1}\)) of \([\text{Ru-bidppz-Ru}]^{4+}\). In principle, in the dinuclear ruthenium complex the \(^3\text{IL}\) state should still lie at higher energy, but due to the uncertainty in determining the triplet state of the bidppz (different metal and broad emission) and due to the low emission quantum yield and long lifetime of the emitting excited state in \([\text{Ru-bidppz-Ru}]^{4+}\), it is likely that the lowest excited state of the dinuclear complex in dichloromethane is indeed the \(^3\text{IL}\) (see Scheme 6.2). The observed emission therefore results from an equilibrium between the \(^3\text{MLCT}\) and the \(^3\text{IL}\) states.

The dinuclear \([\text{Os-bidppz-Os}]^{4+}\), in de aerated dichloromethane solution, emits with maximum at 750 nm and decay time of 16 ns (inset to Figure 6.2, and Table 6.3). This emission remains nearly unchanged under air-equilibrated conditions (15 ns). The emission of \([\text{Os-bidppz-Os}]^{4+}\), occurring at higher energy compared to \([\text{Os(bpy)}_3]^2+\) (717 nm, see Table 6.3), indicates that the emitting excited state in this case is a \(^3\text{MLCT}\) state, with the excited electron localized on the bridging ligand, better electron acceptor than the ancillary
bipyridines. In butyronitrile, the emission of $[\text{Os-bidppz-Os}^{4+}]$ shifts towards the near-infrared region and becomes so weak to prevent an accurate lifetime determination.

![Energy Level Diagram](image)

**Scheme 6.2** Simplified energy level diagram of $[\text{Ru-bidppz-Ru}^{4+}]$ in CH$_2$Cl$_2$. Wavy arrows represent intersystem crossing and internal conversion decays, while continuous arrows represent absorption and radiative decays.

At 77 K in rigid butyronitrile matrix, the emission maxima of $[\text{Ru-bidppz-Ru}^{4+}]$ and $[\text{Os-bidppz-Os}^{4+}]$ are 591 and 730 nm, respectively, being blue shifted compared to the emission recorded at 293 K (Table 6.3). This trend is consistent with the charge-transfer nature of the emitting excited states and the lack of solvent stabilization in rigid matrix. The emission of $[\text{Ru-bidppz-Ru}^{4+}]$ has spectral shape, energy and lifetime (4 μs) similar to those of the mononuclear complexes $[\text{Ru-dppz}]^{2+}$ and $[\text{Ru(bpy)}_3]^{2+}$ (both emitting at ca. 580 nm with lifetime of 5 μs, see Table 6.3), in agreement with an emitting $^3$MLCT state. However, taking into account the similarity with the phosphorescence band and excited state lifetime of the Zn(II) coordinated bidppz (see above), we can not rule out a possible contribution from the $^3$IL state. The emission of the dinuclear osmium complex $[\text{Os-bidppz-Os}^{4+}]$ at low temperature, can be attributed to a $^3$MLCT transition.
6.2.4 Pico- and Microsecond Time-Resolved Transient Absorption Spectra.

In order to investigate the electronic properties of the dinuclear compounds in more detail, transient absorption (TA) spectra were recorded in a large range of time domain.

6.2.4.1 [Ru-bidppz-Ru]^{4+} complex.

Transient absorption (TA) spectra of [Ru-bidppz-Ru]^{4+} in the nano- and microsecond time domain were recorded upon excitation at 460 nm (2 ns FWHM), in deaerated dichloromethane and butyronitrile (Figures 6.5A and 6.5B, respectively). For the bridging ligand bidppz in deaerated acetonitrile, TA spectra were measured in the microsecond time domain, by excitation at 435 nm (2 ns FWHM) (Figure 6.6). The solution contained a large excess of ZnCl₂.

Figure 6.5 (A) Difference transient absorption spectra of [Ru-bidppz-Ru]^{4+} in deaerated CH₂Cl₂ solution, measured at time delays of 0, 3, 6, 9 and 15 μs, respectively (∆λ = 460 nm, 2 ns FWHM). (B) Difference transient absorption spectra of [Ru-bidppz-Ru]^{4+} in deaerated butyronitrile solution, measured at time delays of 0, 200, 400, 600 and 800 ns, respectively (∆λ = 460 nm, 2 ns FWHM).
The ns-TA spectra of \([\text{Ru-bidppz-Ru}]^{4+}\) in butyronitrile show ground-state bleach in the region 380-480 nm and a transient absorption band at 594 nm (Figure 6.5B) that decays with \(\tau\) of ca. 350 ns, following first-order kinetics. This decay time is similar to the emission lifetime in the same solvent (see above). A band, similar to the transient absorption band at 594 nm, is also observed in the steady-state absorption spectrum of the one-electron reduced species \([\text{Ru-bidppz-Ru}]^{3+}\), at 590 nm (Figure 6.3). The transient band is therefore assigned to the absorption of the lowest \(^3\)MLCT excited state, where the electron is mainly localized on a phenazine moiety of the bridging ligand.

In deaerated dichloromethane solution, \([\text{Ru-bidppz-Ru}]^{4+}\) shows the bleach of the ground state between 380 and 480 nm, while an intense transient absorption band arises at ca. 600 nm. The transient absorption band and the bleach of the ground state decay with first-order kinetics and lifetime of about 9 \(\mu\)s, similar to the corresponding emission decay (see above). The profile of the band at 600 nm differs from that of the band at 594 nm observed in butyronitrile. Furthermore, its intensity is higher, as it can be easily seen by the ratio between this absorption and the bleach at 404 nm (3:1 compared to 1:1 in butyronitrile). The different profiles and decay time observed for the TA spectra in butyronitrile and dichloromethane suggest that the lowest excited state is not the same in these two solvents. Interestingly, the TA spectra (Figure 6.6) of the bridging ligand \(\text{bidppz}\), in deaerated acetonitrile solution, show a transient absorption band at 590 nm with shape and order of magnitude of the decay time (\(\tau = 27 \mu\)s) similar to that of the dinuclear ruthenium complex \([\text{Ru-bidppz-Ru}]^{4+}\) in dichloromethane. The long-lived band observed for the ruthenium complex is therefore
assigned to the absorption of the $^3\text{IL (bidppz)}$ state in thermal equilibrium with the emitting $^3\text{MLCT}$ excited state (see Scheme 6.1), consistent with the emission data.

In order to obtain more kinetic information and insight into the mechanism of the processes, $[\text{Ru-bidppz-Ru}]^{4+}$ was further investigated by (sub)picosecond TA spectroscopy.

Picosecond transient absorption (ps-TA) spectra were recorded for the dinuclear complex $[\text{Ru-bidppz-Ru}]^{4+}$ in dichloromethane and in butyronitrile, between 380 and 680 nm, after excitation at 350 nm. Kinetic profiles were probed at 610 nm (transient absorption). The ps-TA spectra and kinetics of $[\text{Ru-bidppz-Ru}]^{4+}$ in dichloromethane and butyronitrile are depicted in Figures 6.7 and 6.8, respectively.

![Figure 6.7](image)

**Figure 6.7.** (A) Difference transient absorption spectra of $[\text{Ru-bidppz-Ru}]^{4+}$ in CH$_2$Cl$_2$ solution, measured at time delays of 0 (baseline), 1, 6, 12 and 36 ps, respectively ($\lambda_{\text{exc}} = 350$ nm, 130 fs FWHM). (B) Kinetic profile of the difference absorbance measured at 610 nm with 1 ps increment delay ($\lambda_{\text{exc}} = 350$ nm, 130 fs FWHM).
Figure 6.8 (A) Difference transient absorption spectra of [Ru-bidppz-Ru]$^{4+}$ in butyronitrile solution, measured at time delays of 0 (baseline), 5, 20 and 30 ps, respectively ($\lambda_{\text{exc}} = 350$ nm, 130 fs FWHM). (B) Kinetic profile of the difference absorbance, measured at 610 nm with 0.1 ps increment delay ($\lambda_{\text{exc}} = 350$ nm, 130 fs FWHM).

The ps-TA spectrum of [Ru-bidppz-Ru]$^{4+}$ in dichloromethane measured 1 ps after the laser pulse shows the bleach of the ground state in the region between 400 and 500 nm and transient absorption with the maximum at 580 nm (Figure 6.7A). The kinetic profile, recorded at 610 nm, shows that the transient absorption band is partially formed by direct excitation within the instrumental rise time and that, subsequently, its intensity further increases in time ($\tau = 16$ ps) due to indirect formation from another excited state (Figure 6.8B). The ratio between the direct and delayed transient formation is ca. 7:3. The bleach at 460 nm decreases with time, suggesting that the excited state absorbing at 580 nm develops from the excited state populated by the absorption of the ground state at 460 nm. The last spectrum recorded at 36 ps has the same profile as the TA spectra in the nanosecond time domain (see above).

The increase in intensity of the transient band at 580 nm is due to a delayed population of the $^3$IL state from the energetically close $^3$MLCT state, which is populated (after intersystem crossing $^1$MLCT$\rightarrow^3$MLCT) upon excitation (see Scheme 6.2). This is in agreement with the decrease of the bleach at 450 nm, that indicates first the population of the $^1$MLCT state and, subsequently, of the $^3$IL state. The possibility of mixing the $^3$IL and $^3$MLCT states, in dichloromethane, is due to the small energy difference between the two states, estimated to 145 cm$^{-1}$. In our investigation no evidence for equilibrium between different MLCT states was gained.\textsuperscript{17}
In butyronitrile, the ps-TA spectrum of $[\text{Ru-bidppz-Ru}]^{4+}$, measured 5 ps after the laser pulse, shows a bleach in the region between 400 and 500 nm and transient absorption band at 590 nm (Figure 6.8A). The shape of this band is different from that observed in dichloromethane, with a profile significantly falling off at 650 nm. The kinetic plot recorded at 610 nm shows that the transient band is formed within the instrumental rise time and remains nearly unchanged during 100 ps after the laser pulse (Figure 6.8B). The different kinetics and profiles observed for the transient band of $[\text{Ru-bidppz-Ru}]^{4+}$, in dichloromethane and butyronitrile suggest that the corresponding excited state is different in the two solvents, in agreement with the observations made in the nanosecond time domain. The ps-TA spectra in butyronitrile are consistent with the direct population of the lowest $^3$MLCT state localized on the bridging ligand that decays to the ground state in the nanosecond time domain. In butyronitrile solution the $^3$MLCT state lies too low in energy (14800 cm$^{-1}$) to allow any population of the higher lying $^3$IL state ($\Delta E > 2000$ cm$^{-1}$) (Scheme 6.3).

![Energy Level Diagram](image)

**Scheme 6.3** Simplified energy level diagram of $[\text{Ru-bidppz-Ru}]^{4+}$ in butyronitrile. Wavy arrows represent intersystem crossing and internal conversion decays, while continuous arrows represent absorption and radiative decays.
6.2.4.2 $[\text{Os-bidppz-Os}]^{2+}$ complex.

Transient absorption (TA) spectra of $[\text{Os-bidppz-Os}]^{2+}$ in deaerated dichloromethane were recorded in the nanosecond time domain upon excitation at 460 nm (Figure 6.9). The ns-TA spectra of $[\text{Os-bidppz-Os}]^{2+}$ strongly differ from those of the analogous ruthenium complex in the same solvent (Figure 6.5A). The bleach of the ground state dominates the region between 400 and 500 nm, while a weak transient absorption is observed at 580 nm (Figure 6.9). The recovery of the ground state, monitored at 480 nm, follows a first-order kinetics with lifetime of 13 ns, similar to the emission decay (see above). The transient absorption band at 580 nm is assigned to the absorption of the lowest-lying $^3\text{MLCT}$ state, with the excited electron mainly localized on the central phenazine part of the bridging ligand. The band at ca. 580 nm has a lower intensity than expected for the absorption of the one-electron-reduced phenazine moiety. This is probably due to its overlap with the bleach of the $^3\text{MLCT}$ bands.

![Difference transient absorption spectra of $[\text{Os-bidppz-Os}]^{2+}$ in deaerated CH$_2$Cl$_2$ solution](image)

Figure 6.9 Difference transient absorption spectra of $[\text{Os-bidppz-Os}]^{2+}$ in deaerated CH$_2$Cl$_2$ solution, measured at time delays of 0, 5, 10, 15 and 20 ns, respectively ($\lambda_{\text{exc}} = 460$ nm, 2 ns FWHM).

Picosecond transient absorption spectra (ps-TA) of $[\text{Os-bidppz-Os}]^{2+}$ in dichloromethane were recorded between 380 and 680 nm, after excitation at 350 nm. Kinetic profiles were probed at 470 nm (bleaching). The ps-TA spectra and kinetics of $[\text{Os-bidppz-Os}]^{2+}$ are depicted in Figure 6.10. The ps-TA spectra are dominated by the bleach at 490 nm (Figure 6.10A). In the visible region no clear transient absorption can be observed. Kinetics plotted at 470 nm shows the appearance of the bleach within the instrumental rise time, that remains nearly unchanged within next 100 ps (Figure 6.10B). The ps-TA spectra of $[\text{Os-bidppz-Os}]^{2+}$ are consistent with the rapid population of the $^3\text{MLCT}$ excited state and its decay to ground state on the nanosecond time scale. Likewise for $[\text{Ru-bidppz-Ru}]^{2+}$ in butyronitrile, the
MLCT excited state lies too low in energy (13300 cm$^{-1}$) to allow population of the $^3$IL state of the bridge (Scheme 6.4).

![Figure 6.10](image)

Figure 6.10 (A) Difference transient absorption spectra of [Os-bidppz-Os]$^{4+}$ in CH$_2$Cl$_2$ solution, measured at time delays of 0 (baseline), 1, 5 and 10 ps, respectively ($\lambda_{\text{exc}} = 350$ nm, 130 fs FWHM). (B) Kinetic profile of the difference absorbance, measured at 470 nm with 0.1 ps increment delay ($\lambda_{\text{exc}} = 350$ nm, 130 fs FWHM).

![Scheme 6.4](image)

Scheme 6.4 Simplified energy level diagram of [Os-bidppz-Os]$^{4+}$ in CH$_2$Cl$_2$. Wavy arrows represent intersystem crossing and internal conversion decays, while continuous arrows represent absorption and radiative decays.
6.2.5 Redox-switching behavior of \([\text{Ru-bidppz-Ru}]^{4+}\)

One of the interesting features of the chosen bridging ligand (bidppz) is that it can undergo a two-electron reduction with formation of a new chemical species that can be reversibly reconverted into the original molecule. Such process depicted in Scheme 6.1 can be investigated by photophysical means. A stable two-electron reduced and protonated species can also be obtained using a chemical reducing agent in a protic medium. The influence of the reduction of the bridging ligand on the emission of the homodinuclear \([\text{Ru-bidppz-Ru}]^{4+}\) complex was then investigated. Furthermore, the cyclic voltammograms of reference \([\text{Ru-dppz}]^{2+}\) and \([\text{Ru-bidppz-Ru}]^{4+}\) in acidified solution were recorded and the spectroscopic properties of \([\text{Ru-bidppz-Ru}]^{2+}\) were studied after protonation of the negatively charged nitrogens of the reduced phenazine moieties.

As already described (see above and Figure 6.3), the UV/Vis absorption spectrum recorded for \([\text{Ru-bidppz-Ru}]^{2+}\) in butyronitrile, within an OTTLE cell, shows in the UV region \(^{1}\)IL transitions of the bipyridine ligands. The visible region exhibits \(^{1}\)MLCT \(d_{\sigma}^*(\text{Ru})\) to \(\pi^*\)(bpy and bidppz) transitions and, at low energy, at 965 nm, a band is assigned to \(\pi^*-\pi^*\) transitions of the reduced, probably planar, bridging ligand. The emission of \([\text{Ru-bidppz-Ru}]^{3+}\) and \([\text{Ru-bidppz-Ru}]^{2+}\) in deaerated acetonitrile was then monitored, within the OTTLE cell, by single photon counting. Upon stepwise reduction to \([\text{Ru-bidppz-Ru}]^{3+}\) and \([\text{Ru-bidppz-Ru}]^{2+}\), the emission observed at 695 nm \((\tau = 150 \text{ ns, in deaerated solution})\) for the parent complex \([\text{Ru-bidppz-Ru}]^{4+}\) becomes completely quenched. This is attributed to efficient electron transfer from the electrochemically reduced phenazine moiety of bidppz to the excited \(\text{Ru}^{III}(\text{bpy}^{2-}\text{})\) unit. The value of the Gibbs energy change associated with the electron transfer process can be estimated from Eq. 6.1 (for \([\text{Ru-bidppz-Ru}]^{3+}\) )

\[
\Delta G^o = E^o(bdppz^{0/-}) - E^o(bpy^{0/-}) - E_0^0 = -1.23 - (-1.80) - 2.14 \text{ eV} < 0 \quad (6.1)
\]

where \(E_0^0\) is the zero-zero excitation energy, that can be evaluated from the emission at 77 K, and \(E^o(bdppz^{0/-})\) and \(E^o(bpy^{0/-})\) are the electrochemical potentials of the ground-state redox couples, with \(E^o(bpy^{0/-})\) denoting the one-electron reduction of the Ru(bpy)\(_2\) moiety. The negative value of the Gibbs energy change, calculated from Eq.6.1, proves that the electron transfer process is thermodynamically allowed.

In order to investigate the redox changes induced by the protonation of the reduced ligand, CVs were recorded for reference \([\text{Ru-dppz}]^{2+}\) and \([\text{Ru-bidppz-Ru}]^{4+}\) in butyronitrile containing one and two, respectively, equivalents of trifluoromethanesulfonic acid. For reference \([\text{Ru-dppz}]^{2+}\), the phenazine-centred reduction of the dppz ligand becomes electrochemically irreversible in the presence of the acid (Figure 6.11).
Figure 6.11 Cyclic voltammograms (ν = 100 mV s⁻¹) of [Ru-dppz]²⁺ (5 × 10⁻⁴ M) recorded at a Pt disk electrode in butyronitrile, Bu₄NPF₆ (10⁻¹ M), in presence (——) and in absence (-------) of one equivalent of CF₃SO₃H.

The CV exhibits indeed a large separation between the reduction of [Ru-dppz]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[Ru-dppz]²⁺ to [Ru-dppz]²⁺ (Table 6.1). Since in absence of the acid [Ru-dppz]²⁺ is reduced to [Ru-dppz]⁺ and re-oxidized at more negative potentials (−1.41 and −1.35 V, respectively, Figure 6.11 and Table 6.1) the protonation clearly has a stabilization effect on the reduced dppz ligand. By contrast, the bpy-centred reduction steps are not very much affected, remaining fully reversible and shifting only by 100 mV to less negative potentials (−1.73 and −1.93 V, compared to −1.80 and −2.06 V in absence of acid); the ruthenium-centred oxidation remains unchanged (+0.95 V), see Table 6.1 and Figure 6.11. The protonized reduction product H[Ru-dppz]²⁺ does not decompose during the cyclic voltammetric scan (ν = 100 mV/s), as testified by the identical $I_{p,c}$ and $I_{p,a}$ peak current values (Figure 6.11). The electrochemical behavior of [Ru-dppz]²⁺ is consistent with chemical reversibility of the coupled reduction/protonation process and its localization on the phenazine nitrogens. Analogous voltammetric response was also observed for dinuclear [Ru-bidppz-Ru]⁴⁺ in acidified butyronitrile. However, the voltammetric peaks associated with the electrochemically irreversible reduction and protonation of the phenazine nitrogen sites become very broad and determination of the cathodic and anodic peak potentials lacks precision (Scheme 6.5).
Homodinuclear Ruthenium(II) and Osmium(II) Bis-DPPZ Complexes

Scheme 6.5 Scheme for the reduction and protonation of [Ru-bidppz-Ru]^{4+}.

Figure 6.12 UV/Vis spectra of [Ru-bidppz-Ru]^{4+} (—) and H_2[Ru-bidppz-Ru]^{4+} (−−) in CH_3CN. Inset: emission spectra of [Ru-bidppz-Ru]^{4+} (—) and H_2[Ru-bidppz-Ru]^{4+} (−−) in CH_3CN (λ_{exc} = 450 nm).

The UV-Vis and emission spectra were recorded for H_2[Ru-bidppz-Ru]^{4+} (see Scheme 6.5 for the structure) produced in situ by electrolysis in acetonitrile solution containing two equivalents of trifluoromethanesulfonic acid, using an OTTLE cell, or by chemical reduction with Zn granules added to an acidified acetonitrile solution of [Ru-bidppz-Ru]^{4+}.

Upon protonation, the absorption spectrum of the reduced dinuclear complex shows almost no change in the MLCT and 1IL bands at 420 - 460 nm (Figure 6.12) and 290 nm (not shown in the figure), respectively, while the band at 965 nm, assigned to the absorption of the reduced central bis(phenazine) system, shifts to higher energy, toward 650 nm (Figure 6.12).
The blue shift is consistent with the stabilization of the highest occupied π level of the doubly reduced bridging ligand upon protonation, as testified by cyclic voltammetry.

For H₂[Ru-bidppz-Ru]⁴⁺, produced by addition of Zn granules to an acidified acetonitrile solution of [Ru-bidppz-Ru]⁴⁺, luminescence is observed at 657 nm (inset to Figure 6.12). Kinetics recorded at single wavelength shows a second-order decay of the emission, with a short component of 160 ns (66 %) and a longer one of 723 ns (34 %) when monitored at 650 nm, and 140 ns (57 %) and 747 ns (43 %) at 600 nm. The biexponential decay is due to the presence in solution of a mixture of H₂[Ru-bidppz-Ru]⁴⁺ and [Ru-bidppz-Ru]⁴⁺, with H₂[Ru-bidppz-Ru]⁴⁺ emitting at higher energy (λ_max < 650 nm) and decay time of about 750 ns. As expected, a shift of the emission from 695 nm for the parent [Ru-bidppz-Ru]⁴⁺ to higher energy upon reduction and protonation of the bridging ligand is observed. The emitting 3MLCT state of H₂[Ru-bidppz-Ru]⁴⁺ indeed must lie at higher energy, since the electron withdrawing character of the phenazine moiety is now destroyed by its reduction and protonation. When H₂[Ru-bidppz-Ru]⁴⁺ was produced by electrolysis in acidified acetonitrile solution within an OTTLE cell no emission could be observed,²⁰ probably due to its weakness. The lack of reductive luminescence quenching in H₂[Ru-bidppz-Ru]²⁺, in contrast to [Ru-bidppz-Ru]²⁺, clearly suggests that the protonation of the reduced bridging ligand stabilizes the negative charge at the central phenazine moieties, in agreement with the electrochemical observations. The reduction / protonation process is reversible and upon addition of H₂O₂ emission at 695 nm is partly recovered.

The [Ru-bidppz-Ru]⁴⁺ complex acts as a remarkable pH-dependent redox-switch, with the emission quenched upon reduction of the bridging ligand and recovered at higher energy after protonation. However, further studies must be performed to determine more quantitatively the recover of luminescence.

6.3 Conclusions

In this Chapter the (spectro)electrochemical and photophysical behavior of two homonuclear ruthenium and osmium complexes [Ru-bidppz-Ru]⁴⁺ and [Os-bidppz-Os]⁴⁺, and the bridging ligand bidppz (bidppz = 1,1'-dipyrido[3,2-a:2',3'-c]phenazin-1,1'-yl)dipyrido[3,2-a:2',3'-c]phenazine) were described. From the time-resolved spectroscopy in the (sub)pico- to microsecond time domains, we have shown that different excited states are responsible for the spectroscopic behavior of the complexes in solvents of different polarity. In particular, for the [Ru-bidppz-Ru]⁴⁺ in butyronitrile the photoexcitation of the complex results in the population of a 3MLCT state lying at a lower energy than the 3IL state of the bridging bidppz ligand, which decays with a lifetime of 350 ns (Scheme 6.3). In deaerated dichloromethane the excitation again initially populates the 3MLCT state that establishes in 16 ps a thermal equilibrium with the slightly lower-lying 3IL state. The interconversion rate
between the $^3\text{MLCT}$ and the $^3\text{IL}$ state therefore corresponds to $k = 6.2 \times 10^{10}$ s$^{-1}$. The emission occurs from the $^3\text{MLCT}$ state, equilibrated with the $^3\text{IL}$ state, and with a lifetime of 9.7 $\mu$s (Scheme 6.2). For the dinuclear osmium compound $[\text{Os-bidppz-Os}]^{4+}$, the $^3\text{MLCT}$ state lies too low in energy to be in equilibrium with the $^3\text{IL}$ state, in analogy to what observed for the ruthenium complex in butyronitrile (Scheme 6.4).

Furthermore, the redox switch behavior of $[\text{Ru-bidppz-Ru}]^{4+}$ is also presented. Upon two-electron reduction, the bidppz ligand becomes planar and acts as quencher of the emission. Upon protonation of the reduced bidppz$^{2-}$ bridge, the negative charge is stabilized and the emission is recovered. These properties of the bidppz ligand classify it as a highly interesting redox- and pH-controllable molecular switch of luminescence, in particular in the field of developing molecular electronics.

6.4 Experimental Section

Materials. Butyronitrile and acetonitrile (Acros), for electrochemical measurements, were dried over CaH$_2$ and freshly distilled under nitrogen prior to use. Spectroscopic grade acetonitrile, dichloromethane, ethanol and methanol (Fluka) were used as received. The supporting electrolyte Bu$_4$NPF$_6$ (Aldrich) was recrystallized twice from ethanol and dried overnight under reduced pressure at 60 °C. The internal standard ferrocene (Aldrich), ZnCl$_2$ (Fluka) and metallic zinc (Merk) were used as received. Trifluoromethanesulfonic acid (Aldrich) was used as received.

The compounds bidppz, $[\text{Ru-bidppz-Ru}]$(PF$_6$)$_4$, $[\text{Os-bidppz-Os}]$(PF$_6$)$_4$ and $[\text{Ru-dppz}]$(PF$_6$)$_4$ were prepared by the group of Prof. Peter Belser (University of Fribourg, Switzerland) according to literature procedures. The doubly protonated complex $\text{H}_2[\text{Ru-bidppz-Ru}]^{4+}$ was prepared in situ by reducing $[\text{Ru-bidppz-Ru}]^{4+}$ with metallic zinc in acidified acetonitrile or acetone. The parent complex (4.6 mg, 2.3 $\times$ 10$^{-3}$ 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 (1g, about 1 mm size) for 15 min, until the orange color turned slightly brownish.

General Techniques. Cyclic 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. The potential control was achieved with a PAR Model 283 potentiostat. All redox potentials are reported against the ferrocene-ferrocenium (Fc/Fc$^+$) redox couple used as an internal standard$^{29}$ ($E_{1/2} = 0.38$ V vs SCE in acetonitrile)$^{30}$ Tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) was used as supporting electrolyte.

UV/Vis and emission spectrophotometric experiments were performed with an optically transparent thin-layer electrochemical (OTTLE) cell$^{27}$ 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 $\times$ 10$^{-4}$ M in the studied complex and contained 3 $\times$ 10$^{-1}$ M Bu$_4$NPF$_6$. 

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UV/Vis spectra were recorded on a Hewlett-Packard 8453 diode-array spectrophotometer. Emission and excitation spectra were recorded on a Spex 1681 spectrophotometer. For the spectroelectrochemical experiments, emission spectra and lifetime measurements (monitored by single photon counting) were performed using an optical fiber 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 repetition rate of 20 Hz. All the emission spectra were corrected for the photomultiplier response.

Time-resolved emission studies were performed at single wavelength, using a continuously tunable (400-700 nm) Coherent Infinity XPO laser as excitation source. The emission light was collected in an Oriel monochromator, detected by a P28 PMT (Hamamatsu), and recorded on Tektronix TDS3052 (500 MHz) oscilloscope. A photodiode was used as external trigger source. Alternatively, a streak camera (Hamamatsu C5680-21), equipped with a M 5677 sweep unit was used, with a continuously tunable (400-700 nm) Coherent Infinity XPO laser as excitation source.

Nanosecond time-resolved absorption spectra were obtained using a setup described previously. The irradiation source was a continuously tunable (400-700 nm) Coherent Infinity XPO laser working at 10 Hz (2 ns FWHM). Excitation laser light was typically less than 5 mJ pulse$^1$. Samples were prepared to have optical density, at the excitation wavelength, of ca. 0.3 in a 1 cm cuvette. For each sample, spectra were measured at not less than 25 different time delays.

Picosecond transient absorption spectra and single wavelength kinetics were measured using a setup described in detail in a previous paper. The laser system was based on a Spectra-Physics Hurricane Titanium Sapphire regenerative amplifier system. The full spectrum setup was based on an optical parametric amplifier (Spectra-Physics OPA 800) as pump. A residual fundamental light from the OPA pump, was used to generate white light that was detected with a CCD spectrograph. The single-wavelength kinetics setup was based on two OPAs, one used for pumping and the other one for probing, and an amplified Si-photodiode for detection. For both setups the OPA was used to generate excitation pulses at 350 nm. The output laser was typically 5μJ pulse$^1$ (130 fs FWHM) with repetition rate of 1 KHz. A circular cuvette (d = 1.8 cm, 1 mm, Hellma) with the sample solution was placed in a home-made rotating ball bearing (1000 rpm) to avoid local heating by the laser beam. The solutions of the samples were prepared to have an optical density at the excitation wavelength of ca. 0.5 in a 1 mm cell. The absorbance spectra of the solutions were measured before and after the experiments. In all cases less than 10% photodecomposition was observed.

Luminescence quantum yields were measured in optically dilute solutions, using [Ru(bpy)$_3$Cl$_2$ in H$_2$O ($\Phi_{em} = 0.028$) as reference emitter. Estimated experimental errors in the reported data are as follows: absorption and emission maxima ± 2 nm, emission lifetimes 8%, emission quantum yields ± 20%. Where required, deaerated solutions were prepared by freeze-pump-thaw technique on a vacuum line.
Homodinuclear Ruthenium(II) and Osmium(II) Bis-DPPZ Complexes

References