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Synthesis and Photochemical Properties of Ru^{II} and Ru^{II}-Os^{II} Complexes with a Long Bridging Ligand of Tetrapyridobiphenazine

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Semi rigid tetradentate π-conjugated bridging ligand, tetrapyridobiphenazine (tpbpz), its mono and binuclear complexes of ruthenium(II) and ruthenium(II)-osmium(II) have been synthesized. The ligand has chelation sites separated by 2.1 nm. Photochemical properties of these complexes have been investigated using time-resolved laser spectroscopy. In the Ru^{II}-Os^{II} heteronuclear complex, intramolecular energy transfer occurs from a metal-to-ligand charge transfer (MLCT) state of the Ru^{II} moiety, *i.e.*, (^{3}CT)Ru, to the second metal site, *i.e.*, Os^{II}. Molar absorption coefficient differences ($\Delta\varepsilon_{es}$) along with the excited state formation were determined using an energy transfer method from the triplet metal-to-ligand charge transfer state (^{3}MLCT) of the complex to anthracene. Quantitative conversion of Ru^{II}-Os^{II} compound to Ru^{II}-Os^{III} was performed by means of electrochemistry.

Keywords
photochemical property
Ru-Os complexes

INTRODUCTION

Photoinduced electron transfer and energy transfer processes cover a wide range of fundamental natural phenomena such as photosynthesis[1] as well as a variety of applications[2] in modern science and technology. Recently, much attention has been paid to the synthesis of polynuclear compounds, with the purpose of investigating current theoretical treatments[3] of electron transfer and designing molecular devices performing useful light-induced functions.[4] Several Ru^{II} and Os^{II} polypyridyl complexes exhibit suitable excited state and redox properties to play the role of building blocks for the construction of photoactive supramolecular systems.[5] Intramolecular photoinduced electron transfer in Ru^{II}-Os^{III} mixed valence complexes has been studied by Nozaki *et al.*[6] A Ru^{II}-Os^{III} binuclear complex exhibits several excellent advantageous properties as central units for the study of electron transfer reactions. For example, Ru^{II}-Os^{III} binuclear complexes possess chemical and photochemical stability. Os^{II} in the photoproduct state, Ru^{III}-Os^{II}, can act as a chromophore and thus enable a multistep photoinduced electron transfer system.

Photoexcitation of the Ru^{II} site results in formation of a lowest energy metal-to-ligand charge transfer excited state of triplet spin multiplicity (^{3}MLCT). The ^{3}CT then undergoes an electron-transfer reaction between Ru^{II} and Os^{III}, which is denoted as forward electron-transfer (FET) (Eq. 2). The product is a mixed valence (MV) isomer of the reactant. The Ru^{III}-Os^{II} state finally goes back to the ground state through a backward electron-transfer

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(BET) (Eq. 3). An energy transfer (EnT) competes with the forward electron transfer (FET).

$$\mathrm{Ru^{II}\text{-}Os^{III}} \xrightarrow{h\nu} \mathrm{(^3CT)Ru^{II}\text{-}Os^{III}} \qquad (1)$$

$$\mathrm{(^3CT)Ru^{II}\text{-}Os^{III}} \xrightarrow{\mathrm{FET}} \mathrm{Ru^{III}\text{-}Os^{II}} \qquad (2)$$

$$\mathrm{Ru^{III}\text{-}Os^{II}} \xrightarrow{\mathrm{BET}} \mathrm{Ru^{II}\text{-}Os^{III}} \qquad (3)$$

$$\mathrm{(^3CT)Ru^{II}\text{-}Os^{III}} \xrightarrow{-h\nu'} \mathrm{Ru^{II}\text{-}Os^{III}} \qquad (4)$$

$$\mathrm{(^3CT)Ru^{II}\text{-}Os^{III}} \xrightarrow{\mathrm{EnT}} \mathrm{Ru^{II}\text{-}(^3CT)Os^{III}} \longrightarrow \mathrm{Ru^{II}\text{-}Os^{III}} \qquad (5)$$

Rates of FET and BET in such donor-acceptor complexes joined by a bridging ligand mainly depend on the donor-acceptor distance, free energy of reaction, energy and shape of high energy occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the bridging ligand. The various energy levels of excited state and product state with respect to the ground state play a vital role for the interpretation of electron-transfer rates. The formation efficiency of the mixed valence isomer state for such a donor-acceptor compound is closely related to the rate of FET and rates of other deactivation processes,[7] two of which are shown in Eqs. (4) and (5). In Ru^{II}-Os^{III} compounds bridged by an alkyl chain or tetrapyridophenazine (tpphz), the FET yields were found to be 0.4–0.5,[6] because the FET rate might compete with energy transfer to low lying ligand-to-metal charge transfer (LMCT) state of the Os^{III} site (Eq. 5). Although the intervening groups of Ru^{II}-Os^{III} compounds are completely different from each other, the short distances of Ru-Os compounds (1.2–1.5 nm) are responsible for the fast rates of FET, BET and EnT. It is evident from such compounds that the electron transfer process of the $(^3CT)Ru^{II}$-Os^{III} to Ru^{III}-$(^3CT)Os^{II}$ state may compete with the energy transfer from $(^3CT)Ru^{II}$ to a triplet LMCT excited state of Os^{III} through quenching.[6b] Dipole-dipole interactions are considered to play a dominant role for slow energy transfer within donor-acceptor compounds containing heavy metal ions such as Ru^{II} (Ref. 8) and Os^{II} (Refs. 9, 10). The distance between the two metal sites influences the energy transfer rate more strongly than the electron transfer rate.[11] In addition to these d^6 metal compounds, the photophysical study on other d^{10} metals such as Cu^{I} (Ref. 12) and Pt^{0} (Ref. 13) compounds has recently attracted increasing attention among the researchers.

In this study, an attempt has been made to find a suitable compound in which a fast and highly efficient FET occurs and the electron transfer (ET) product state is fairly stable. A π-conjugated semi rigid tetradentate bridging ligand, tetrapyridobiphenazine (tpbpz), along with its mono and binuclear complexes have been synthesized [14] where the chelation sites are separated by 2.1 nm. Photochemical properties and thermal stability of Ru^{II}, Ru^{II}-Ru^{II} and Ru^{II}-Os^{II} compounds with the tpbpz ligand were investigated using time-resolved laser spectroscopy. The difference in the molar absorption coefficient ($\Delta\varepsilon_{es}$) along with the excited state formation were determined using an energy transfer reaction from the ^{3}MLCT state to anthracene. This is necessary for the determination of the ET yields for such complex/es. Further study is under way for the synthesis of other Ru^{II}-Os^{III} compounds of tetrapyridobiphenazine (tpbpz) with different substituents of bipyridine (bpy) coordinating to the Ru^{II} ion.

EXPERIMENTAL

Materials and Instrumentation

Acetonitrile (AN) was purified by fractional distillation from P_2O_5 after being kept one day over molecular sieve 4A. Butyronitrile (BN) was distilled over P_20_5 under reduced pressure. All other solvents [dichloromethane (DCM), dimethylformamide (DMF), dimethylsulphoxide (DMSO), *etc.*] were of analytical grades. Requisite compounds were synthesized and other chemicals of quality grades were used as supplied.

Absorption spectra were measured on a Shimadzu Spectrophotometer (UV-2500 PC). Emission spectra were recorded using a grating monochromator (Jasco CT 25-C) with a photodiode image sensor (Hamamatsu C4351). The detector sensitivity was corrected using a bromine lamp (JPD 100 V 500 WCS). The sample was excited using a YVO_4 laser (532 nm, 20 mV). The system of nanosecond kinetic spectroscopy was reported elsewhere.[15] The redox potentials of metal complexes were measured by differential pulse voltammetry using a dc pulse polarograph (Huso, HECS – 312B). Voltamograms were recorded using a platinum disk electrode (diameter 0.5 mm) in a solution of the complexes containing 0.05 mol dm^{-3} tetra-n-butyl ammonium perchlorate. All spectroscopic data were obtained by dissolving in spectral grade solvents.

Synthesis

Tetrapyrido biphenazine (tpbpz). – A mixture of ground 3,3'-diaminobenzidine (48 mg) and 1,10-phenanthroline-5,6-dione ($phenO_2$, 96 mg) in ethanol (20 ml) was refluxed for 2 hours. The resulting yellowish green product was collected by filtration. Purification was done by recrystallization from a mixture of acetonitrile, water and a few drops of hydrochloric acid for several times. The resulting product was dried under vacuum overnight. Yield: 80 mg.

$[(bpy)_2Ru(tpbpz)](PF_6)_2 \cdot H_2O$ (Figure 1). – $PhenO_2$ (10 mg) and 3,3'-diaminobenzidine (10 mg) were refluxed in DMF (4 ml) for 30 minutes. The resulting brownish product was filtered, dried and treated with $[(bpy)_2Ru(phenO_2)](PF_6)_2$ (24 mg) in a mixture of acetonitrile and acetic acid (volume ratio 1:1) at 100 °C for 3 hours. The crude red product was purified chromatographically over a LH Sephadex column

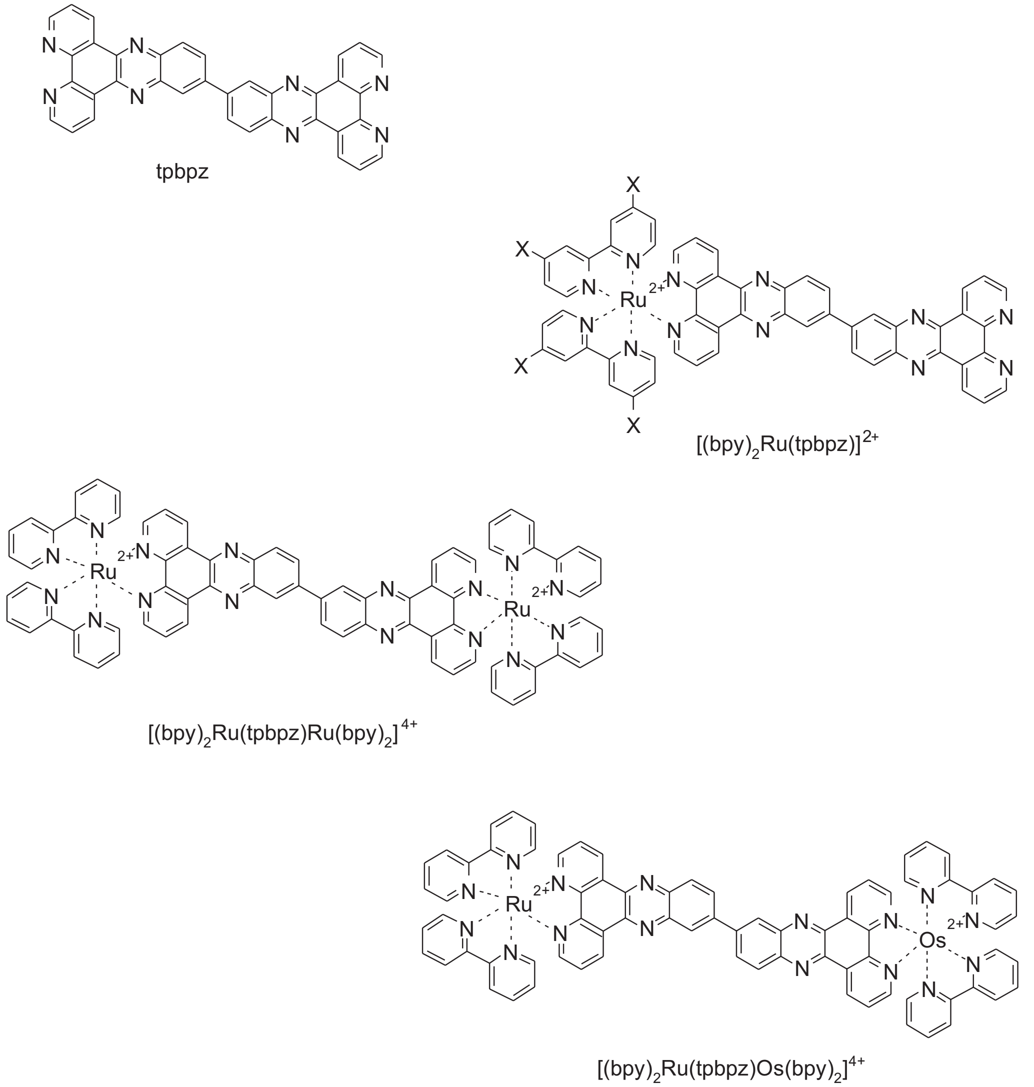

Figure 1. Structural formulae of tpbpz, [(bpy)$_2$Ru(tpbpz)]$^{2+}$, [(bpy)$_2$Ru(tpbpz)Ru(bpy)$_2$]$^{4+}$ and [(bpy)$_2$Ru(tpbpz)Os(bpy)$_2$] $^{4+}$.

using a mixture of acetonitrile and methanol (vol. ratio, ψ = 1:1) as eluent. Recrystallization for further purification was done with a mixture of methanol and water (ψ = 1:1). The red product obtained was dried under vacuum overnight. Yield: 12 mg.

Anal. Calcd. for [(bpy)$_2$Ru(tpbpz)](PF$_6$)$_2$ · H$_2$O: C 52.36, N 13.09, H 2.80 %. Found: C 52.30, N 13.00, H 3.27 %.

[(bpy)$_2$Ru(tpbpz)Ru(bpy)$_2$](PF$_6$)$_4$ · 4H$_2$O (Figure 1). – To a hot solution of tetrapyrido biphenazine (20 mg) in ethylene glycol (5 ml), Ru(bpy)$_2$Cl$_2$ (48 mg) was added. After heating at 180 °C for about 10 minutes, water and aqueous NH$_4$PF$_6$ solution were added for precipitation. The crude red product separated was purified chromatographically over CM Sephadex C 25 using a mixture of acetonitrile and aqueous buffer as eluent. The desired red band was eluted at pH = 5.7 containing 25 mmol dm^{-3} NH$_4$PF$_6$.

Recrystallization was done in ethanol-water (ψ = 1:1). The red product obtained was dried under vacuum overnight. Yield: 18 mg.

Anal. Calcd. for [(bpy)$_2$Ru(tpbpz)Ru(bpy)$_2$](PF$_6$)$_4$ · 4H$_2$O: C 44.68, N 10.97, H 2.84 %. Found: C 44.55, N 10.90, H 2.93 %.

ESI mass spectrum: *m/z* calculated for [M-2PF$_6$]$^{2+}$ 839.45, [M-3PF$_6$]$^{3+}$ 511.31, [M-4PF$_6$]$^{4+}$ 347.24. Found: 839.50, 511.40, 347.30, respectively {M = [(bpy)$_2$Ru(tpbpz)-Ru(bpy)$_2$](PF$_6$)$_4$}.

[(bpy)$_2$Ru(tpbpz)Os(bpy)$_2$](PF$_6$)$_4$ · 8H$_2$O (Figure 1). – [(bpy)$_2$Ru(tpbpz)](PF$_6$)$_2$ (12 mg) and Os(bpy)$_2$Br$_2$ (10 mg) were mixed in ethylene glycol (2 ml) and refluxed (180 °C) for about 10 minutes. Water and aqueous NH$_4$PF$_6$ solution were added for precipitation. The crude brownish product separated was purified chromatographically over CM Sephadex C 25 using a mixture of acetonitrile and aqueous buffer as eluent. The desired brownish band was eluted at pH = 5.7 containing 25 mmol dm^{-3} NH$_4$PF$_6$. Purification was done by adding a mixture of acetone and water followed by evaporation and addition of aqueous NH$_4$PF$_6$ solution. Lastly, the brownish precipitate separated out was washed with water and dried under vacuum. Yield: 18 mg.

Anal. Calcd. for $[(bpy)_2Ru(tpbpz)Os(bpy)_2](PF_6)_4 \cdot 8H_2O$: C 41.45, N 10.17, H 2.99 %. Found: C 41.07, N 10.17, H 2.99 %.

RESULTS AND DISCUSSION

Absorption Spectra

Absorption spectra of $[(bpy)_2Ru(tpbpz)](PF_6)_2$, $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$ and $[(bpy)_2Ru(tpbpz)Os(bpy)_2](PF_6)_4$ are shown in Figure 2. Intraligand transitions (π-π*) of bipyridine (bpy) occurred at 285 nm and those of tetrapyridobiphenazine (tpbpz) occurred at 310–320 nm and 400–410 nm, respectively. Metal-to-ligand charge transfer (MLCT) band was observed at around 430–460 nm for all these Ru^{II} complexes. In the case of $[(bpy)_2Ru(tpbpz)Os(bpy)_2](PF_6)_4$, a LMCT band was observed in the region from 550 to 700 nm due to the transition from ligand π-orbital to dπ orbital of the Os^{III} ion.[6b]

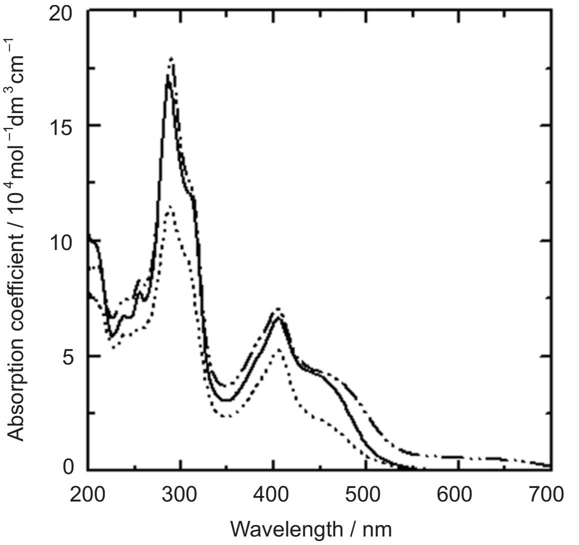

Figure 2. Absorption spectra of $[(bpy)_2Ru(tpbpz)](PF_6)_2$ (·····), $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$ (——) and $[(bpy)_2Ru(tpbpz)Os(bpy)_2](PF_6)_4$ (–··–) in AN at RT.

Emission Spectra

Emission spectra of the mono and binuclear complexes of Ru^{II} at room temperature (RT) and 77 K are shown in Figures 3 and 4, respectively. Emission peak energies of $[(bpy)_2Ru(tpbpz)](PF_6)_2$ and $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$ in various solvents at room temperature and in glassy BN at 77 K are given in Table I. In dichloromethane, highest peak energies of about 15600 cm^{-1} were observed for both $[(bpy)_2Ru(tpbpz)](PF_6)_2$ and $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$ whereas peak energies were shifted to 12900 cm^{-1} and 12400 cm^{-1} in dimethylsulphoxide, respectively. In acetonotrile, both complexes showed a moderate shift of peak energy.

In the case of $[(bpy)_2Ru(tpbpz)Os(bpy)_2](PF_6)_4$, a weak emission peak was observed at around 16000 cm^{-1} while an intense peak was observed at around 13700 cm^{-1} in glassy BN at 77 K (Figure 4 inset). Weak emission from the Ru^{II} parts indicates that the fast intramolecular energy transfer to Os^{II} parts occurred in the Ru^{II}-Os^{II} heterodinuclear complex.

It is well-known that $E_{peak} = E_{o\text{-}o} - \lambda_{in} - \lambda_{out}$, where E_{peak}, $E_{o\text{-}o}$, λ_{in} and λ_{out} stand for the maximum emission peak energy, energy of ^{3}MLCT state, intramolecular reorganization energy and solvent reorganization energy, respectively. As for the emission spectra in BN at 77 K, the very negligible contribution of λ_{out} made the peak energy value closer to the $E_{o\text{-}o}$ value. At room tempera-

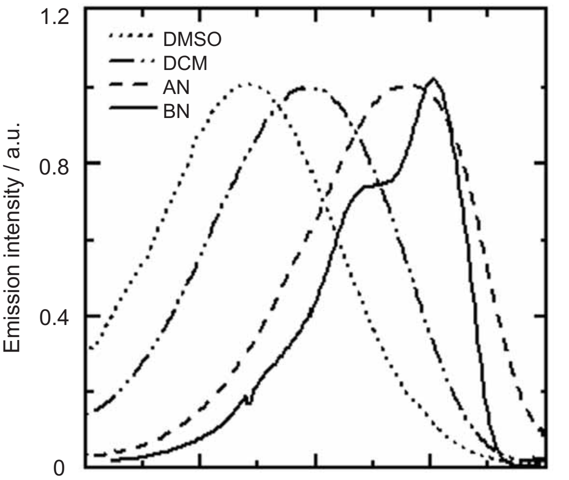

Figure 3. Emission spectra of $[(bpy)_2Ru(tpbpz)](PF_6)_2$ at RT and at 77 K in BN (solid line).

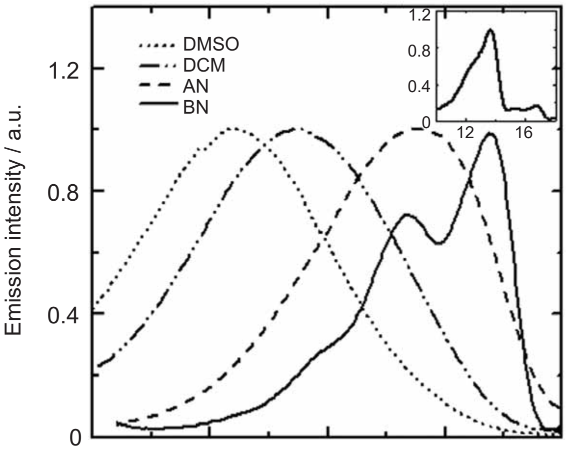

Figure 4. Emission spectra of $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$ at RT and 77 K (BN) and $[(bpy)_2Ru(tpbpz)Os(bpy)_2](PF_6)_4$ in BN at 77 K (inset).

TABLE I. Emission peak energy of the compounds in various solvents

Compound	Peak energy at RT / 10^3 cm^{-1}			Peak energy at 77 K / 10^3 cm^{-1}
	AN$^{(a)}$	DMSO$^{(a)}$	DCM$^{(a)}$	BN$^{(a)}$
$[(bpy)_2Ru(tpbpz)]^{2+}$	13.9	12.8	15.6	16.02, 15.06 ($\Delta^{(b)}$ = 0.96)
$[(bpy)_2Ru(tpbpz)Ru(bpy)_2]^{4+}$	13.5	12.4	15.6	16.77, 15.37 ($\Delta^{(b)}$ = 1.4)
$[(bpy)_2Ru(tpbpz)Os(bpy)_2]^{4+}$				16.75, 15.16 ($\Delta^{(b)}$ = 1.59) 13.60, 12.95 ($\Delta^{(b)}$ = 0.69)

$^{(a)}$ AN-acetonitrile, BN-butyronitrile, DCM-dichloromethane, DMSO-dimethylsulphoxide.
$^{(b)}$ Difference in peak energy between first and second energy peaks.

ture, λ_{out} has a considerable effect on the total emission peak energy. It was observed that the peak energy varied greatly from DCM to DMSO. The extents of solvent shifts were 2700 cm^{-1} and 3200 cm^{-1} for $[(bpy)_2Ru(tpbpz)](PF_6)_2$ and $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$, respectively (Table I). Considerable red shifts of the emission in AN were observed at RT: 2120 cm^{-1} for $[(bpy)_2Ru(tpbpz)](PF_6)_2$ and 3270 cm^{-1} for $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$ when compared with those in glassy BN at 77 K.

Redox Potentials

Ru^{II} complexes showed reversible one electron metal based oxidation processes corresponding to the Ru^{III}/Ru^{II} couple. Oxidation potentials of Ru^{II} complexes were within the range from 0.90 V to 0.92 V against the Fe$^+$/Fe couple. Redox potentials of the complexes are given in Table II.

As the reduction potentials were ligand based, it had to be ascertained which of the two ligands, nonbridging bpy or bridging tpbpz, took part in the first reduction. The first reduction potentials of $[(bpy)_2Ru(tpbpz)](PF_6)_2$ and $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$ were about 1.1 V, which was about 600 mV less than that of $[Ru(bpy)_3](ClO_4)_2$ (1.7 V), indicating that the first reduction took place on the bridging ligand, tpbpz. This revealed that the photo-excited electron was located on the bridging ligand (tpbpz$^{\cdot-}$). Elliott *et al.*[16] have reported this kind of phenomena in complexes of such type. Reduction potentials observed at –1.3 V to 2.5 V in similar types of complexes were ascribed to the reduction of ligands.[17] Such reductions are found to be solvent dependent. The first oxidation of the Ru^{II}-Os^{II} heterodinuclear complex occurred at Os^{III}, which was followed by oxidation of Ru^{II}. Oxidation potential of this complex was within the range from 0.47 V to 0.92 V against the Fe$^+$/Fe couple (Figure 5). These types of redox potentials of metal-based oxidations in mono and binuclear complexes suggest that they may be classified as class I mixed valent compounds.[18]

Transient Absorption Spectra

Nanosecond transient absorption spectra of $[(bpy)_2Ru(tpbpz)](PF_6)_2$ and $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$ were observed following the laser excitation at 532 nm. In the case of $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$, the absorption band at 340 nm might be due to π-π* transition of tpbpz. Bleaching of π-π* transition of tpbpz around 410 nm signified the conversion of tpbpz to (tpbpz)$^-$ in the excited

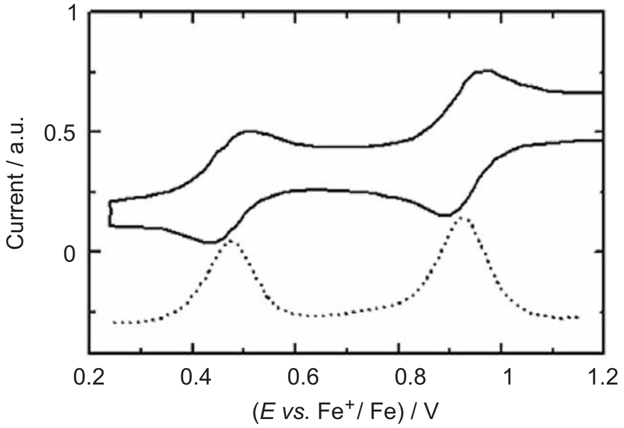

Figure 5. Cyclic voltamogram and differential pulse voltamogram of $[(bpy)_2Ru(tpbpz)Os(bpy)_2](PF_6)_4$ in AN containing 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$.

TABLE II. Redox potentials$^{(a)}$

Compound	E°(III/II) / V	E°(II/I) $^{(b)}$ / V
$[(bpy)_2Ru(tpbpz)]^{2+}$	0.905	–1.150 –1.570 –1.815
$[(bpy)_2Ru(tpbpz)Ru(bpy)_2]^{4+}$	0.920	–1.155 –1.395 –1.805
$[(bpy)_2Ru(tpbpz)Os(bpy)_2]^{4+}$	0.47 0.92	–1.108 –1.410 –1.705

$^{(a)}$ Values were obtained in ACN at RT.
$^{(b)}$ E°(II/I) values were obtained against Cp$^+$ / Cp.

state. A transition band around 600 nm can be assigned to π-π* transition of tpbpz ligand anion coordinating to Ru^{III} (Figure 6). The same trend is followed for $[(bpy)_2Ru(tpbpz)](PF_6)_2$ (Figure 6). The decay constants (k_d) of $[(bpy)_2Ru(tpbpz)](PF_6)_2$ and $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$ were 1.69×10^6 s^{-1} (Figure 7) and 4.50×10^6 s^{-1} whereas their excited state lifetimes were about 600 ns and 200 ns, respectively. As the decay constants of transient absorptions at any wavelength and the decay constants of emission around 600–660 nm for each of the mononuclear and binuclear complexes of Ru^{II} (Figure 8) were comparable and followed single exponential decay, no photoproduct state or intermediate state was formed. Bleaching of MLCT band around 450 nm and the broad band around 600 nm in the nanosecond transient absorption spectra indicate the existence of the lowest ^{3}MLCT excited state in the complex.[11] Therefore the lowest excited state is assigned as ^{3}MLCT.

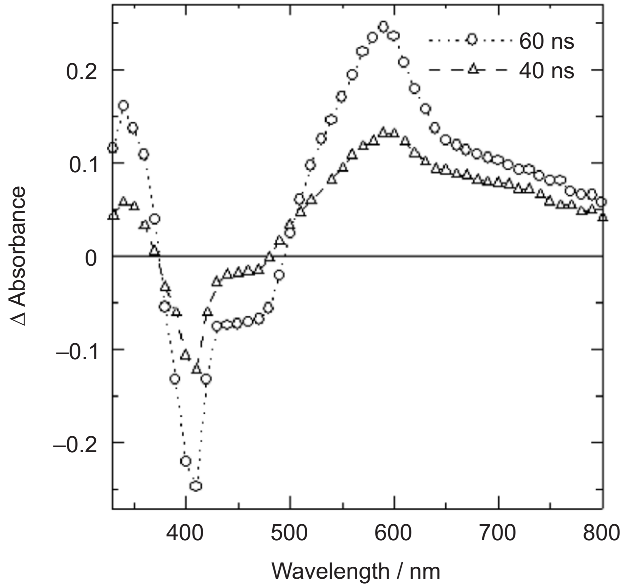

Figure 6. Transient absorption spectra of $[(bpy)_2Ru(tpbpz)](PF_6)_2$ (60 ns) and $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$ in AN (40 ns).

Waterland *et al.*[19] reported that dipyrodophenazine (dppz) complexes of ruthenium, *i.e.*, Ru^{II}dppz, have two closely lying solvent dependent excited states named ^{3}MLCT1 and ^{3}MLCT2, which involve higher energy unoccupied orbitals mainly centered on the phenanthroline part of dppz and the lowest unoccupied orbital on the phenazine part of dppz, respectively. The solvent shift of emission for Ru^{II}tpphz complexes provides a strong indication that the lowest emitting excited state involves the tpphz ligand.[20,21] For the tpbpz complexes, the issue of the location of the lowest unoccupied molecular orbital (LUMO) of tpbpz either on phenanthroline part (MLCT1) or phenazine part (MLCT2) needs to be addressed. Lower redox potential and a large solvent shift of emission energy provided a hint in favor of tpbpz localization. In addition, the appearance of a broad band around 600 nm and the absence of any band at 370 nm in the nanosecond transient absorption spectra of $[(bpy)_2Ru(tpbpz)](PF_6)_4$ and $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$ indicate that the LUMO was mainly localized on the phenazine part of the bridging ligand, tpbpz.

Molar absorption coefficient differences ($\Delta\varepsilon_{es}$) of the excited state for $[(bpy)_2Ru(tpbpz)](PF_6)_4$ and $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$ have also been determined using the method of energy transfer from ^{3}MLCT to anthracene (A). This method was considered to be an efficient energy transfer method for these complexes.[15]

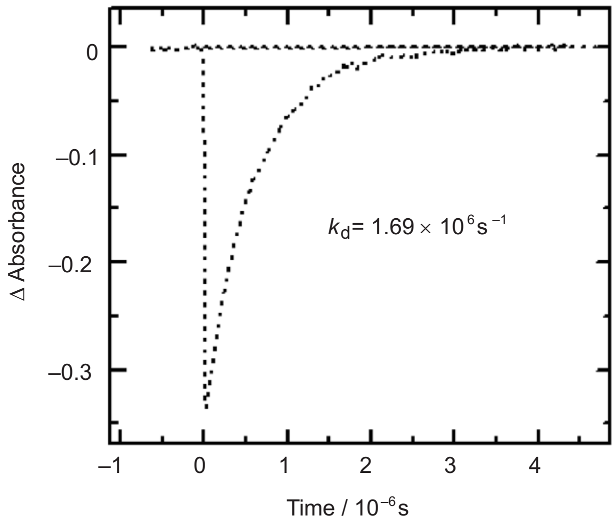

Figure 7. Transient absorption decay of $[(bpy)_2Ru(tpbpz)](PF_6)_2$ at 410 nm in AN.

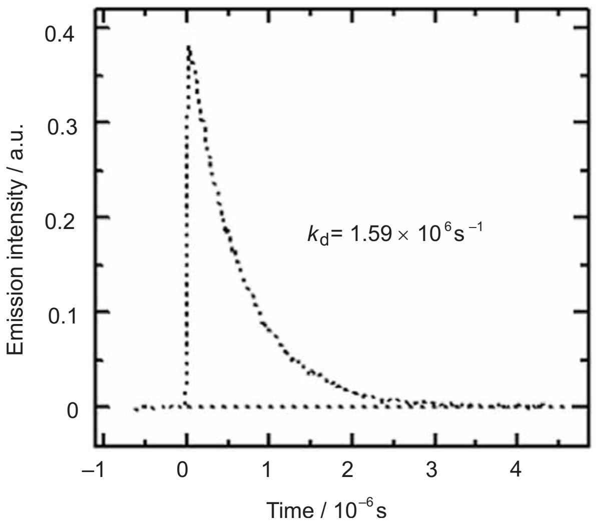

Figure 8. Transient emission decay of $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$ at 660 nm in AN.

Determination of $\Delta\varepsilon_{es}$ by Energy Transfer from ^{3}MLCT to Anthracene

THEORY:

$$^3\text{Ru} + \text{A} \xrightarrow{k_{\text{en}}} \text{Ru} + {}^3\text{A} \tag{6a}$$

$$^3\text{Ru} \xrightarrow{k_{\text{d}}} \text{Ru} \tag{6b}$$

Solving (6a) and (6b), we get:

$$[^3\text{A}]_{t=\infty} = \frac{k_{\text{en}}[\text{A}]_\text{o}}{k_{\text{en}}[\text{A}]_\text{o} + k_\text{d}}[^3\text{Ru}]_\text{o} \text{ (when } t = \infty) \tag{7}$$

The observed rate constant (k_{obs}) for the ^{3}Ru state is given as:

$$k_{\text{obs}} = k_{\text{en}}[\text{A}]_\text{o} + k_\text{d} \tag{8}$$

and the reaction yield of energy transfer (F_q) is defined as:

$$F_q \equiv \frac{k_{\text{en}}[\text{A}]_\text{o}}{k_{\text{en}}[\text{A}]_\text{o} + k_\text{d}} = \frac{k_{en}[\text{A}]_\text{o}}{k_{\text{obs}}} \tag{9}$$

Finally, we get:

$$[^3\text{A}]_{t=\infty} = F_q[^3\text{Ru}]_\text{o} \tag{10}$$

PROCEDURE:

- Determination of k_{en} according to equation (3)
- Determination of $[^3\text{A}]_{t=\infty}$ from $\left\langle \dfrac{\Delta\text{abs}_{421}}{44700(\varepsilon_{421})} \right\rangle$
- Final determination of Δ absorbance and $\Delta\varepsilon_{\text{es}}$ according to equation (10)

Standard solutions of anthracene (1, 2, 3, *etc.* mmol dm^{-3}) were prepared. Emissions of each solution were measured after mixing the same volume of $[(\text{bpy})_2\text{Ru}(\text{tpbpz})](\text{PF}_6)_2$ solutions (0.02 mmol dm^{-3}). The decay constants observed for three of the solutions are 7.28 × 10^6 s^{-1} (1 mmol dm^{-3} A), 9.72 × 10^6 s^{-1} (2 mmol dm^{-3} A), and 1.58 × 10^6 s^{-1} (without A). From the slope of graph (k_{obs} *vs.* $[\text{A}]_\text{o}$), we got the k_{en} value according to Eq. (8) A plot of $^3[\text{A}]_{t=\alpha}$ *vs.* F_q was made for these three solutions and the value of $[^3\text{Ru}]_\text{o}$ was found according to Eq. (10) Finally, we calculated the $\Delta\varepsilon_{\text{es}}$ values at two different wavelengths (410 nm and 600 nm) from this concentration of triplet ruthenium, $[^3\text{Ru}]_\text{o}$ (Table III). Nanosecond transient absorption spectra and the transient absorption rise at 421 nm (due to anthracene) of $[(\text{bpy})_2\text{Ru}(\text{tpbpz})](\text{PF}_6)_4$ in the presence of anthracene are shown in Figures 9 and 10, respectively.

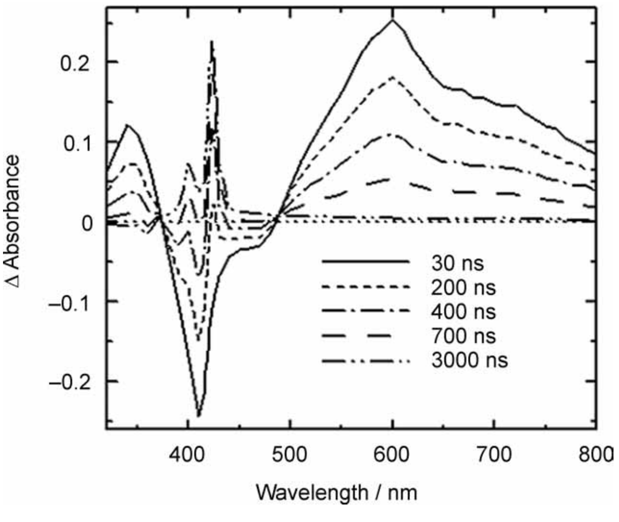

Figure 9. Transient absorption spectra of $[(\text{bpy})_2\text{Ru}(\text{tpbpz})](\text{PF}_6)_2$ with anthracene in AN.

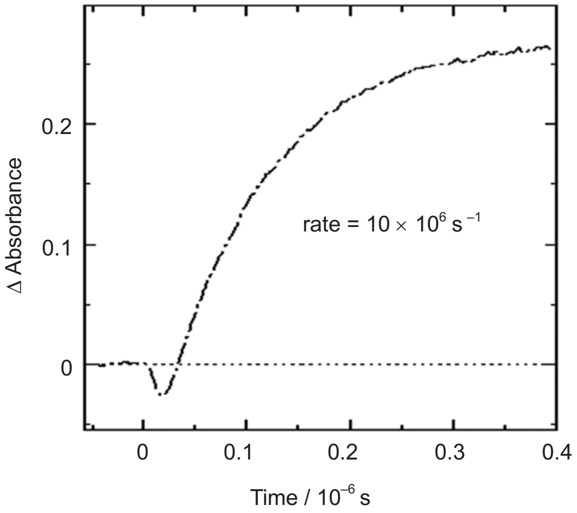

Figure 10. Transient absorption rise of $[(\text{bpy})_2\text{Ru}(\text{tpbpz})](\text{PF}_6)_2$ with anthracene in AN at 421 nm.

TABLE III. Determination of $\Delta\varepsilon_{\text{es}}$ using the energy transfer method for $[(\text{bpy})_2\text{Ru}(\text{tpbpz})](\text{PF}_6)_2$

$\frac{[\text{A}]_\text{o}}{\text{mmol dm}^{-3}}$	$\frac{k_{\text{obs}}}{10^6\text{s}^{-1}}$	$\frac{\Delta\text{abs}_{421}}{\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}}$	$\frac{[^3\text{A}]_\infty{}^{(a)}}{\mu\text{mol dm}^{-3}}$	F_q	$\frac{[^3\text{Ru}]_\text{o}}{\mu\text{mol dm}^{-3}}$	$\frac{\Delta\text{abs}_{410}}{\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}}$	$\frac{\Delta\text{abs}_{600}}{\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}}$	$\Delta\varepsilon_{410}{}^{(b)}$	$\Delta\varepsilon_{600}{}^{(c)}$
0	1.58					–0.302	+0.167		
1	7.28	0.328	7.34	0.78	9.41	–0.149	+0.163	–15800	+17300
2	9.72	0.270	6.04	0.84	7.19	–0.112	+0.117	–15600	+16300

$^{(a)}$ $[^3\text{A}]_\infty = \dfrac{\Delta\text{abs}}{44700}$, $^{(b)}$ $\Delta\varepsilon = \dfrac{\Delta\text{abs}_{410}}{[^3\text{Ru}]_\text{o}}$, $^{(c)}$ $\Delta\varepsilon = \dfrac{\Delta\text{abs}_{600}}{[^3\text{Ru}]_\text{o}}$

TABLE IV. Determination of $\Delta\varepsilon_{es}$ for $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$

$\frac{[A]_o}{mmol\ dm^{-3}}$	$\frac{k_{obs}}{10^6 s^{-1}}$	$\frac{\Delta abs_{421}}{mol^{-1} dm^3 cm^{-1}}$	$\frac{[^3A]_\infty{}^{(a)}}{\mu mol\ dm^{-3}}$	F_q	$\frac{[^3Ru]_o}{\mu mol\ dm^{-3}}$	$\frac{\Delta abs_{410}}{mol^{-1} dm^3 cm^{-1}}$	$\frac{\Delta abs_{600}}{mol^{-1} dm^3 cm^{-1}}$	$\Delta\varepsilon_{410}{}^{(b)}$	$\Delta\varepsilon_{600}{}^{(c)}$
0	4.28					–0.299	+0.264		
1	8.53	0.148	3.31	0.50	6.62	–0.112	+0.108	–16900	+16300
2	10.53	0.216	4.83	0.58	8.33	–0.130	+0.121	–15600	+14500

$^{(a)}\ [^3A]_\infty = \frac{\Delta abs}{44700}$, $^{(b)}\ \Delta\varepsilon = \frac{\Delta abs_{410}}{[^3Ru]_o}$, $^{(c)}\ \Delta\varepsilon = \frac{\Delta abs_{600}}{[^3Ru]_o}$

The same procedure was followed in the case of the binuclear complex, $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$ (Table IV). Thus, we determined the molar absorption coeficient differences of the excited state for $[(bpy)_2Ru(tpbpz)](PF_6)_4$ and $[(bpy)_2Ru(tpbpz)Ru(bpy)_2](PF_6)_4$ using the energy transfer method from ^{3}MLCT to anthracene. These differences are essential in determining the ET yield of the Ru^{II}-Os^{III} complex.

A novel, long, semi-rigid and π-conjugated tetradentate bridging ligand, tpbpz, its mono and binuclear complexes of Ru^{II} and Ru^{II}-Os^{II} were synthesized and their photochemical properties were investigated. Based on the long lifetime (about 200–600 ns) of the ^{3}MLCT excited state, big transient absorption change (MLCT bleaching at 450 nm and a broad band at around 600 nm) and reversible redox behavior, these complexes are found to be chemically stable and suitable for the study of photoinduced electron transfer processes. Our further study on the electrochemical synthesis of Ru^{II}-Os^{III} and determination of their FET, BET rates and ET yields by pico and sub-pico second laser photolysis using $\Delta\varepsilon_{es}$ is in progress.

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SAŽETAK

Sinteza i fotokemijska svojstva Ru^{II} i Ru^{II}-Os^{II} kompleksa s dugim premostujućim tetrapiridobifenazinskim ligandom

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Sintetizirani su polukruti tetradentatni π-konjugirani premostujući ligand, tetrapiridobifenazin (tpbpz), i njegovi mono i bi-nuklearni kompleksi s rutenijem(II) i rutenij(II)-osmijem(II). Ligand ima kelatna mjesta koja su razmaknuta za 2,1 nm. Fotokemijska svojstva ovih kompleksa su istraživana pomoću vremenski odijeljene laserske spektroskopije. U Ru^{II}-Os^{II} heteronuklearnom kompleksu, intramolekularni prijenos energije se dešava metal-ligand prijenosom naboja (MLCT) s Ru^{II} centra, tj. (^{3}CT)Ru na drugi metalni centar, tj. Os^{II}. Razlika u molekularnom apsorpcijskom koeficijentu ($\Delta\varepsilon_{es}$) za vrijeme stvaranja pobuđenog stanja je određena korištenjem metode prijenosa energije s triplet metal-ligand prijenosom naboja (^{3}MLCT) s kompleksa na antracen. Kvantitativna konvezija Ru^{II}-Os^{II} spoja u Ru^{II}-Os^{III} je postignuta elektrokemijski.