

Novel Ru(II)/Os(II)-Exchange Homo- and Heterometallic Polypyridyl Complexes with Effective Energy Transfer

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Two novel homometallic Ru–Ru and heterometallic Ru–Os dimers and trimers, $[M^{II}(bpy)_2(4-tpy-4'-methyl-2,2'-bipyridine) M^{II}(tpy)]^{4+}$ and $[M^{II}(bpy)_2](4-tpy-4'-tpy-2,2'-bipyridine)(M^{II-}(tpy))_2]^{6+}$, have been first prepared and characterized. Electrochemical properties of the metal-based reversible oxidation and ligand-based reduction are measured. Spectroscopic analysis of these complexes exhibits for every Ru- or Os-based subunit an individual intense absorption spectrum extended over the entire UV and visible region. The heteronuclear complexes

Introduction

Information transfer at the molecular level is an emerging area in the field of molecular photonics and has been studied extensively.^[1] Hence much attention has been focused on welldefined distance and elaborated structures, in particular bidentate or tridentate ruthenium(II) and osmium(II) mixedmetal complexes, and significant progress has been achieved in mono-, di-, and trinuclear Ru(II) and Os(II) polypyridyl complexes.^[2] Based on the progress in light- and/or redoxinduced electron conversion and energy transfer, these complexes have been widely applied in various areas of luminescent sensors and photocatalysts.^[3] Among these polymetallic complexes, the unfavorable properties of bis-tridentate Ru(II) complexes are weak luminescence and short excited-state lifetime at room temperature. These deficiencies in terpyridine Ru(II) complexes severely limits their application as photosensitizers.^[3c,4] Therefore, tpy-type complexes have been replaced by bpy-tpy-type (bpy=2,2'-bipyridine, tpy=2,2':6',2''terpyridine) complexes or substituted tpy-type complexes or variation of the bound metal centers,^[5] providing directional control of the photoinduced intercomponent processes between metal-to-ligand charge-transfer (³MLCT) and metal-centered (³MC) state.^[2d,6] Intramolecular energy transfer takes place from the Ru(II)-based center to the lowest ³MLCT excited state

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 $[Ru^{II}(bpy)_{2}(4-tpy-4'-methyl-2,2'-bipyridine)Os^{II}(tpy)]^{4+}, \qquad [Ru^{II-}(bpy)_{2}](4-tpy-4'-tpy-2,2'-bipyridine)(Os^{II}(tpy))_{2}]^{6+}, and \qquad [Os^{II-}(bpy)_{2}](4-tpy-4'-tpy-2,2'-bipyridine)(Ru^{II}(tpy))_{2}]^{6+} display a weak emission spectrum in the near-infrared region (NIR). The luminescence of the polynuclear assemblies is quantitatively quenched, by intramolecular energy transfer to the lower-lying metal-to-ligand charge transfer (³MLCT) and metal-centered (³MC) state of the Os(II)-based center or Ru(II)-terpyridine moiety at room temperature.$

of the Os(II)-based center to provide a multichannel optical sensor. $\ensuremath{^{[7]}}$

In this work, two series of metal exchange multinuclear [M^{II}(bpy)₂-(4-tpy-4'-methyl-2,2'-bipyridine)-M^{II-} compounds, $[M^{\parallel}(bpy)_2]$ - (4-tpy-4'-tpy-2,2'-bipyridine)-(M^{\parallel} - $(tpy)]^{4+}$ and $(tpy))_2]^{6+}$ (M=Ru, Os; depicted in Scheme 1 and Scheme 2), were synthesized and systematically investigated. The synthesized ligands have a π -conjugated bidentate-tridentate (bpy-tpy) group, which accounts for the superiority of the constructed homo- and heteronuclear complexes. The innovation of this study is the arrangement of coordinated metals [Ru^{II}(bpy)₂-Os^{II}tpy was replaced by Os^{II}(bpy)₂-Ru^{II}tpy], which provides the opportunity to demonstrate the interrelationship of different combinations of metal centers. The coordination of Os(II)terpyridine centers in heteronuclear complexes shows an additional ³MLCT absorption band that extends over the entire visible spectrum.^[3c] Furthermore, these complexes are donorbridge-acceptor systems, where the Ru(II) moiety serves typically as the energy donor, while either the Ru(II)-terpyridine or the polypyridyl Os(II) moiety acts as the acceptor site. These systems are in principle capable of undergoing intracomponent energy transfer and are suitable for investigating the mechanism of photoinduced intramolecular energy and/or electron transfer.

In the following, optical processes are discussed, especially with respect to energy and/or electron transfer, based on excitation absorption spectroscopy, as donor–acceptor systems exhibit non-radiative spectra. The main objective of this study was to selectively excite the Ru(II)-bipyridine fragment and to analyze the energy transfer to a low-energy state of either the Ru(II)-terpyridine or polypyridyl Os(II) center. Our results provide insight into the properties of donor–bridge–acceptor groups for future development of artificial photochemical switches and biological sensors.





Scheme 1. Chemical structures of the target complexes bearing a single terpyridine moiety on the ligand (labeled with S).



Scheme 2. Chemical structures of the target complexes bearing two terpyridine moieties on the ligand (labeled with D).

Results And Discussion

Synthesis of ligands L¹ and L²

The ligands 4-tpy-4'-methyl-2,2'-bipyridine (L^1) and 4-tpy-4'-tpy-2,2'-bipyridine (L^2) were synthesized in a two step reaction. The methyl group of 2,2'-bipyridine was changed into formyl group

by oxidation with selenium dioxide. 4-Formyl-4'-methyl-2,2'bipyridine and 4,4'-diformyl-2,2'-bipyridine were reacted with 2acetylpyridine to obtain the corresponding ligands. Both L^1 and L^2 ligands have not been reported before and configuration of mixed bidentate (bipyridine) and tridentate (terpyridine) bridge.



Synthesis of Polynuclear Complexes

The mono-, homo- and heteroleptic complexes derived from the ligands L^1 and L^2 define two novel classes of complexes. The mononuclear key complexes bear one or two free terpyridine sites that can react with appropriate metallic precursors (Ru-/Os-tpy). In the synthesis of the binuclear complexes, a mononuclear complex was used as a second ligand to react with the metallic monomer or introducing a combination of metallic ions and the terpyridine motif. The resulting complexes were converted into their hexafluorophosphate salts by anion exchange after column chromatography (silica gel: MeCN-saturated KNO₃-H₂O) and characterized by elemental (C, H, and N) analyses, ¹H NMR, and HRMS, as described in the Experimental Section.

¹H NMR and HRMS Characterization of the Complexes

The ¹H NMR spectra of the obtained metal complexes in DMSOd₆ and presented in Figures S1–S11 (Supporting Information). Many peaks of the obtained complexes were extensively overlapped owing to the symmetry of the bpy-tpy and bpy-(tpy)₂ bridging ligand. As whole protons can be hardly assigned to the correct position in the metal combination groups, the spectra were characterized based on the coupling constants and chemical shift values. The assignment of the different peaks of **D–Ru–Ru** was realized by performing {¹H–¹H} COSY spectra (Figure S12). Because of the electron-withdrawing effect of the Ru(II), the chemical shifts of the bpy (3H, 9.96 ppm) and tpy (3"H and 5"H, 9.79 ppm) groups on the ligand L² were markedly downfield shifted, while that of the tpy (5'H and 5"'H, 7.32 ppm) group was upfield shifted for **D–Ru–Ru**.

All obtained compounds were also characterized by highresolution mass spectrometry (HRMS) in MeCN. The mass spectra of all the derivatives complexes are shown in Figures S13–S23. The mass spectra recorded for all synthesized complexes exhibit typical features of successive loss of the PF₆⁻ counterions of the Ru-/Os-polypyridyl complexes, and the detected preferable mass peaks are in very good agreement with the theoretically calculated values. For example, the characteristic peak of **D**–**Ru**–**Ru** (m/z) assigned to [M–6(PF₆)]⁶⁺ is calculated as 283.7110 and detected at 283.7120, that assigned to [M–5(PF₆)]⁵⁺ is calculated as 369.4460 and detected at 369.4471, that assigned to [M–4(PF₆)]⁴⁺ is calculated as 498.0486 and detected at 498.0500, and that assigned to [M–2(PF₆)]²⁺ is calculated as 1141.0613 and detected at 1141.0651.

Electrochemical Characterization

All polypyridine complexes were electrochemically characterized by cyclic voltammetry (CV) and/or differential pulse voltammetry (DPV). The oxidation processes were studied in MeCN solution, while the reduction processes were studied in DMF solution (5×10^{-4} M, 0.1 M Bu₄NClO₄) at a scan rate of 100 mV s⁻¹ at room temperature using a platinum auxiliary electrode, a saturated potassium chloride calomel reference electrode, and a microcell equipped with a platinum disk working electrode. The extracted electrochemical characteristics of all here prepared complexes as well as some relevant mononuclear reference compounds are collected in Table 1 for comparison. CV and DPV of the two trimetallic complexes **D–Os–Ru** and **D–Ru–Ru** are shown in Figure 1, while all other compounds are depicted in Figures S24 and S25.

For the monometallic complexes, the reversible oneelectron oxidation at 1.29 V (S-Ru) and 1.33 V (D-Ru) can be assigned to the Ru^{II}/Ru^{III} couple, and the reversible one-electron oxidation at 0.87 V (S-Os) and 0.89 V (D-Os) can be assigned to the Os^{II}/Os^{III} couple. Similarly, the binuclear complexes **S**–**Ru–Os** and S-Os-Ru revealed two metal-based reversible oxidations at 1.31 and 1.35 V (of Ru(bpy) and Ru(tpy), respectively) and at 0.86 and 0.98 V [of Os(bpy) and Os(tpy), respectively]. The homonuclear complexes S-Ru-Ru shows a single two-electron oxidation at 1.34 V, and D-Ru-Ru exhibits a single threeelectron oxidation at 1.36 V. In the heteronuclear trimetallic complexes, one single-electron oxidation of D-Os-Ru at 0.90 V can be attributed to the Os-based subunit, and a single twoelectron oxidation at 1.34 V can be attributed to the Ru-based subunit. D-Ru-Os exhibited a single-electron oxidation at 1.37 V (Ru^{II}/Ru^{III}) and a two-electron oxidation at 0.98 V (Os^{II}/ Os^{III}). Compared with the oxidation peaks of the reference

Table 1. Electrochemical CV and/or DPV data of all complexes. ^[a]					
Compound	Oxidation [V]	Reduction [V]			
[Ru(bpy)3]2 + [b] [Os(bpy)3]2 + [c] [Ru(tpy)2]2 + [b] [Os(tpy)2]2 + [d] S-Ru S-Os S-Ru-Os S-Ru-Os S-Ru-Os S-Ru-Ru D-Ru D-Ru D-Os	1.29 0.85 1.30 0.97 1.29 0.87 0.98, 1.31 0.86, 1.35 1.34 1.33 0.89	$\begin{array}{c} -1.30, -1.54, -1.75\\ -1.20, -1.41, -1.77\\ -1.24, -1.49\\ -1.23, -1.52\\ -1.16, -1.40, -1.63\\ -1.12, -1.32, -1.60\\ -0.92, -1.24, -1.36, -1.48, -1.68\\ -0.88, -1.19, -1.32, -1.44, -1.70\\ -0.92, -1.24, -1.52\\ -0.80, -1.08, -1.36, -1.56, -1.72\\ -0.80, -1.04, -1.28, -1.52, -1.76\end{array}$			
D–Ru–Os D–Os–Ru D–Ru–Ru	0.98, 1.37 0.90, 1.34 1.36	-0.88, -0.96, -1.20, -1.36, -1.52 -0.84, -1.00, -1.20, -1.36, -1.48 -0.88, -0.96, -1.24, -1.36, -1.52			

[a] The oxidation processes were analyzed from CV, and the reduction processes were analyzed from DPV. [b] From ref. [11a] [c] From ref. [11b] [d] from ref. [11c]



Figure 1. CV and DPV oxidation processes of the complexes D–Os–Ru and D–Ru–Ru (a); DPV reduction processes of the complexes D–Os–Ru and D–Ru–Ru (b).



Table 2. Luminescence and UV–Vis absorption spectral data of all complexes.									
Compound	Absorption, $\lambda max [nm] (104\epsilon/M-1 cm^{-1})$						Luminescence, 298 K λmax [nm] T [ns] 10–34		
[Ru(bpy) ₃] ^{2+[a]}	255(0.35)	287(6.44)	451(1.05)				620	1100	60.0
$[Ru(tpy)_2]^{2+[c]}$	271(2.43)	308(4.45)	474(1.05)				629	0.25	\leq 0.05
[Os(bpy) ₃] ^{2+[b]}	254(0.68)	290(7.71)	434(0.99)	472(0.94)	575(0.30)		719	49	3.2
$[Os(tpy)_2]^{2+[c]}$	232(0.68)	271(2.63)	312(5.86)	474(0.98)	548(0.47)	660(0.29)	718	269	14.0
S—Ru	245(4.56)	288(7.18)	457(1.38)				627	226	57.2
S–Os	215(8.70)	291(7.48)	484(1.29)	645(0.34)			736	/	3.76
S—Ru—Os	240(6.26)	288(11.06)	308(8.23)	497(4.01)	663(0.67)		812	/	3.28
S–Os–Ru	241(5.00)	291(9.09)	306(6.94)	513(3.33)	634(0.6)		_[d]	/	_[d]
S–Ru–Ru	241(3.75)	288(6.56)	306(4.96)	501(2.23)			706	120(τ ₁); 376(τ ₂)	2.64
D–Ru	240(6.39)	286(7.01)	309(3.75)	466(1.26)			645	304	82.4
D–Os	214(7.19)	239(5.76)	290(6.39)	370(1.24)	450(1.36)	498(1.25)	768	/	3.20
D-Ru-Os	212(21.65)	276(10.09)	284(10.34)	310(11.10)	505(5.21)	671(1.14)	816	/	3.48
D–Os–Ru	239(8.72)	273(10.47)	291(11.76)	307(12.22)	517(5.53)		833	/	2.44
D–Ru–Ru	209(11.62)	274(9.98)	283(10.74)	307(10.54)	504(5.48)		703	126(τ_1); 346(τ_2)	7.52
[a] From ref [18a]. (b) τ from ref [20]. Φ from ref [2a]. λ measured in this work [c] τ and Φ from ref [3c]. λ measured in this work except for [Bu(try)_2] ²⁺ (from									

[a] From ref. [18a], [b] τ from ref. [20], Φ from ref. [2a], λ measured in this work. [c] τ and Φ from ref. [3c], λ measured in this work except for [Ru(tpy)₂]²⁺ (from ref. [2b]. [d] Intensity too low for measurement.

complexes listed in Table 1, our mononuclear and heteronuclear complexes exhibited relatively higher oxidation potentials because the better π^* electron acceptor property of the bridging ligands stabilizes the metal based HOMO, making the oxidation of metal more difficult.^[8]

Multiple-step reductions of the mono- and heteronuclear complexes were revealed by DPV measurements. As a noncoordinated terpyridine ligand can be reduced twice,^[2b] the five successive reduction processes of the mononuclear complexes D-Ru and D-Os include the two reduction processes of the two non-coordinated terpyridine dyads. In addition, S-Ru and S-Os undergo three reduction processes of the two bipyridine moieties and one bipyridine-based ligand, and the homonuclear complex S-Ru-Ru only exhibited three weak reduction processes. As the reduction potential of $[Ru(bpy)_3]^{2+}$ (-1.24 V) is more negative than that of $[Ru(tpy)_2]^{2+}$ (-1.16 V), the coordinated terpyridine ligands are reduced before the bipyridine ligands in the bipyridine-bridge-terpyridine systems. Hence among the five sequential reduction peaks of the multinuclear complexes S-Ru-Os, S-Os-Ru, D-Ru-Os, D-Os-Ru, and D-Ru-Ru, the first and third negative potentials are related to the terpyridine moieties, while the other three negative potentials are ascribed to the three bipyridine moieties.

In comparison, the oxidation process of the Ru^{II}/Ru^{III} couple occurs at a slightly more positive potential than that of the Os^{II}/ Os^{III} couple, as the occupied $d\pi$ orbitals of Os(II) have a higher energy than those of Ru(II).^[2g,9] The first two reduction processes of all acquired complexes are shifted to positive potentials compared with those of the reference compounds because the presence of the terpyridine units in the bridging ligands significantly stabilizes the ligand π^* orbitals.^[10] The presence of one oxidation process for two peripheral terpyridine moieties in the trimetallic complexes indicates that the two terpyridine coordination sites have equal energies in the coordination systems.

Photophysical Characterization

Both UV–Vis and fluorescence spectroscopy of the prepared complexes were carried out in MeCN solution at a concentration of 10^{-5} M at room temperature. The data collected from these spectra are shown in Table 2, and the spectra are presented in Figure 2.

In the monometallic complexes S-Ru and D-Ru, the spectral region with moderately intense peaks around at 460 nm is linked to metal $d\pi(Ru) \rightarrow ligand \pi_1^*$ charge transfer (MLCT), while the strong absorption band at 288 nm is due to $\pi_1 \rightarrow \pi_1^*$ spin-allowed ligand-centered transition (LC).^[3b] A similar absorption profile was observed for the Os-based mononuclear complexes S-Os and D-Os. The Os-based complexes S-Os, S-Ru-Os, S-Os-Ru, and D-Ru-Os exhibited not only a ¹MLCT band in the same wavelength range as the Ru(II) ¹MLCT transitions but also a weak ³MLCT absorptions in the visible region at 645-670 nm, which stem from the spin-forbidden 1 [Os^{II}(d π)⁶] to 3 [Os^{II}(d π)⁵tpy-ligand(π *)¹] transition.^[2g,3c,12] The absorption of the multi-metallic complexes in the range of 497-517 nm is ascribed to the $d\pi$ (Ru and Os) \rightarrow tpy ligand of L¹ and L² ¹MLCT transitions. The trinuclear compounds D-Ru-Os, D-Os-Ru, and D-Ru-Ru showed strong intense bands at 275 nm and 280-290 nm, which is reasonably close to bipyridine-based ligand-centered (LC) transitions (the absorption at



Figure 2. Absorption spectra for (a) bpy-typ-type complexes and (b) bpybitpy-type complexes in acetonitrile.



275 nm is assigned to the two bipyridine groups, while that at 280–290 nm corresponds to the bipyridine group of the ligand) and the LC absorption of the two terpyridine units at 307–310 nm. The detected terpyridine-based LC transition clearly suggests that both terpyridine groups have the same energy, which is in agreement with their electrochemical properties. Finally, the weak absorption of **D**–**Os** in the UV region at about 370 nm reflects the electron transfer from the $\pi_{\rm M}$ to $\sigma_{\rm M}^*$ orbitals, indicating a metal-centered (MC) excited state transition.

In comparison with the model molecules and their substituted pyridine analogues,^[13] the ¹MLCT transitions of the synthesized trinuclear complexes are shifted to lower energies (at ~517 nm, $\varepsilon = 5.5 \times 10^4$ M⁻¹ cm⁻¹), and the stabilization of the π^* orbitals of the terpyridine moieties results in higher absorptivity. Consequently, the trimetallic systems are expected to be an ideal light absorption sensitizer because of their broad absorption ranges and high molar absorptivities.

The excitation wavelengths of all complexes at 450 nm as well as their luminescence profiles are compiled in Table 2. The uncorrected and the normalized luminescence spectra (inset) are depicted in Figure 3. The Ru-based monomeric compounds **S–Ru** and **D–Ru** exhibited strong luminescence bands at 627 and 645 nm, respectively, while the Os-based moieties of **S–Os** and **D–Os** showed much weaker bands at 736 and 768 nm, respectively. In the Os(II) complexes, because the energy gap of ³MLCT/³MC is much higher than in the analog Ru(II) complexes, the deactivation of the excited state is from ³MLCT to the ground state (GS), resulting in an emission of weaker and much longer wavelengths.^[3c,14]

The observed weak luminescence band of both di- and trinuclear complexes matches well with the typical of $M(d\pi) \rightarrow$ bpy/tpy(π^*) ³MLCT excited state emission.^[15] It is proposed that the excited state deactivation are involved in the radiative and nonradiative decay of MLCT state as well as the internal conversion to a higher-lying ³MC state of dd orbital at room temperature. Nevertheless, the Ru(II)-terpyridine-type complexes have adopted a six-coordinated structure and turned their ideal octahedral geometry into a distorted spatial structure makes the ³MLCT state energy gradually approach the ³MC level.^[16] The similarity of the ³MLCT/³MC energies allows the deactivation via a ³MC state rather than via a radiative decay from the ³MLCT state to the ground state, resulting in Ru(tpy)-

type complexes with less intense or non-luminescence at room temperature. $\ensuremath{^{[17]}}$

The homonuclear compounds exhibit shoulders and longerwavelength luminescence at 706 nm for S-Ru-Ru and at 703 nm for D-Ru-Ru, which are both remarkably red-shifted relative to the luminescence of their precursors $[Ru(bpy)_3]^{2+}$ (612 nm) and [Ru(tpy)₂]²⁺ (629 nm). The luminescence spectra of the heteronuclear complexes are substantially shifted to the near-infrared region (NIR), the related Ru/Os dyads and triads well documented in literatures previously, however, 1.Ru₂Os (780 nm), $[(bpy)_2Os(tpphz)Os(bpy)2]^{4+}$ and $[(bpy)_2Os(tpphz)]^{4+}$ Os(bpy)2]4+ (790 nm) are in the visible region.^[18] Showing a weak emission band at 812 nm for S-Ru-Os, at 816 nm for D-Ru-Os, and at 833 nm for D-Os-Ru. The measured luminescence originated from the ³MLCT state of the Os^{II}-center, resulting in entirely quenched luminescence emission in the Ru-Os triads by the Os^{II}-center.^[2g] The Ru^{II}-tpy or Os(II) excited state emission indicates that energy transfer occurs in the metal donor-acceptor complexes, which will be discussed in detail in the next section. Furthermore, the emission intensity of S-Os-Ru is too weak or has a too short lifetime to be monitored accurately at room temperature.

In order to analyze more luminescence properties, luminescence quantum yield and lifetime were also characterized. The luminescence lifetimes of S–Ru, S–Ru–Ru, D–Ru, and D–Ru–Ru were measured in MeCN solution at a concentration of 10^{-5} M at room temperature. S–Ru and D–Ru showed relatively longer lifetimes of 226 and 304 ns, respectively, while S–Ru–Ru and D–Ru–Ru showed lifetimes of 144 and 159 ns (average lifetime of the entire decay), respectively. The corresponding decay profiles are shown in Figure 4. The luminescence quantum yields (Φ) were calculated according to Equation (1), as previously reported by Demas and Crosby:^[19]

$$\Phi_{\rm c} = (A_{\rm c}/A_{\rm s})(I_{\rm c}/I_{\rm s})(\eta_{\rm c}/\eta_{\rm s})^2 \Phi_{\rm s} \tag{1}$$

where **c** and **s** stands for compounds of synthesized and standard complex, η is the refractive index of the solvent, A is the solution absorbances at the excitation wavelength (λ_{ex}), I are the integrated emission intensities, respectively, and Φ_s is the standard luminescence quantum yield of $[Ru(bpy)_3]^{2+}$ ($\Phi = 0.06$).



Figure 3. Photoluminescence spectra for (a) bpy-tpy-type complexes and (b) bpy-bitpy-type complexes in acetonitrile at room temperature, inset is the normalized photoluminescence spectra.



Figure 4. Photoluminescence decays of S–Ru, S–Ru–Ru, D–Ru, and D–Ru–Ru in acetonitrile at room temperature.



Intramolecular Triplet Energy Transfer in Multimetallic Complexes

In the preceding demonstration, weak luminescence was detected for the homoleptic ruthenium(II) complexes S-Ru-Ru and **D-Ru-Ru**, which is consistent with noticeable Ru^{II}(bpy)-Ru^{II}(tpy) interactions through the bpy-tpy bridging ligand. Due to the lowest energy of the ³MLCT (Ru-tpy) excited state, allowing the potentially emitting ³MLCT (Ru-bpy) excited state transfer to ³MLCT (Ru-tpy) excited state. Ru(tpy)₂-type complexes exhibit a low energy gap between the ³MLCT excited state and the ³MC state, the photoinduced energy intercrossing (³MLCT-³MC) is finally non-radiatively guenched to the ground state (GS). The theoretical primary energy level of the transmission process is illustrated in Scheme 3a, the energy transmission can take place by through space coulombic interaction (Förster) and electron exchange (Dexter).^[21] The rate constant for the intracomplex energy transfer (κ_{en}) was computed based on Equation (2) to be 3.9×10^6 s⁻¹ for S–Ru–Ru and 4.6×10^6 s⁻¹ for D-Ru-Ru:

$$\kappa_{en} = (1/\tau) - (1/\tau^0)$$
 (2)

where τ is the lifetime of **S**–**Ru**–**Ru** (τ_1 : 120 ns) and **D**–**Ru**–**Ru** (τ_1 : 126 ns), and τ^0 is the lifetime of **S**–**Ru** (226 ns) and **D**–**Ru** (304 ns).

The trimetallic complexes containing $[Ru(bpy)_3]^{2+}$ and $[Os-(tpy)_2]^{2+}$ moieties displayed a relatively weak luminescence with emission at low energies at room temperature, while the precursor $[Ru(bpy)_3]^{2+}$ exhibited an intense luminescence. The weak emission could be an indication for a straight-forward

energy transfer between the connected metal centers. In the case of the binary mixed-metal complexes **S–Ru–Os** and **D–Ru–Os**, the energy absorption of Ru-bpy in the visible region indicates a ¹MLCT excited state, which rapidly converts into a potentially emitting ³MLCT excited state. Because of the lower energy of the ³MLCT (Os-tpy) level, energy transfer from the ³MLCT (Ru-bpy) excited state to the lower energy Os-based state is facilitated, which can be monitored by the characteristic ³MLCT (Os-tpy) long-wavelength emission. Furthermore, the ³MLCT excited state partially interconverts into the ³MC state, facilitating nonradiative decay back to the GS (Scheme 3b).

The trinuclear systems **S–Os–Ru** and **D–Os–Ru** based on the $[Os(bpy)_3]^{2+}$ and $[Ru(tpy)_2]^{2+}$ motifs have the weakest luminescence intensity among all complexes. This is possibly due to the transfer of the excited state from the ¹MLCT (Ru-tpy) state of the periphery with weak emission to the lower energy ³MLCT (Os-bpy) excited state as well as concurrently to the ³MC (Os-bpy) state (Scheme 3c).

Theoretical Computations

Great efforts were taken to optimize the geometrical and photophysical performance of coordination compounds based on density functional theory (DFT) applying the B3LYP functional.^[22] The electron density and orbital energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO, LUMO+1, LUMO+2) of all compounds are summarized in Table 3. The HOMO and the LUMOs of **D**–**Ru**–**Ru** are shown in Figure 5, and all other



Scheme 3. Energy Level Mechanism of the Emissive State of Multinuclear Compounds D–Ru–Ru (a), D–Ru–Os (b), and D–Os–Ru (c), where the straight line represents excitation; the dotted line represents luminescence; and the wavy line represents radiationless decay.



Table 3. Calculated HOMO and LUMO energies of the ligands and related compounds.							
Compound	EHOMO	ELUMO	ELUMO + 1	ELUMO + 2			
	[eV]	[eV]	[eV]	[eV]			
L ¹ L ² S-Ru S S-Ru-Os S-Os-Ru S-Ru-Ru D-Ru D-Ru D-Os D-Ru-Os	-6.88 -6.83 -6.15 -5.83 -6.17 -5.92 -6.23 -6.22 -5.90 -6.07	-2.21 -2.28 -2.88 -3.24 -3.28 -3.26 -3.03 -3.10 -3.42	-1.83 -2.17 -2.73 -2.73 -2.98 -2.94 -2.93 -2.77 -2.81 -3.24	-1.64 -1.89 -2.68 -2.67 -2.91 -2.93 -2.87 -2.71 -2.70 -3.04			
D–Os–Ru	-6.08	-3.46	-3.25	-3.01			
D–Ru–Ru	-6.37	-3.44	-3.25	-2.99			



Figure 5. Graphical illustration of the electron densities of the HOMO and the LUMOs of the D–Ru–Ru homonuclear complex.

compounds containing ligand L^1 and L^2 are presented in Figures S26–S36.

The orbital diagrams show that the HOMO of the mononuclear species is entirely located on the coordinated metal center, while the bimetallic compounds is primarily localized on the metal of the bipyridine units. The electronic structures of these two species are a consequence of the oxidation processes of the metal centers (M^{II}/M^{III}, M=Ru, Os), as indicated by the electrochemical measurements. In the trinuclear complexes **D**–**Ru**–**Os** and **D**–**Os**–**Ru**, the HOMO is almost entirely localized on the Os^{II} centers. In addition, the HOMO of the homonuclear complex **D**–**Ru**–**Ru** is nearly equally distributed over the three Ru^{II}-centers, which is in agreement with the electrochemical measurements. The LUMOs of the mononuclear and binuclear complexes are concentrated at the bpy ligand, which is similar to the sequential ligand-centered reduction processes observed in the electrochemical experiments. Notably, the LUMOs of the trimetallic complexes are usually delocalized over the whole bridging ligand, thus exhibiting low ¹MLCT absorption bands in the visible region around 500 nm, as revealed by the spectroscopic analysis.

Conclusion

Homometallic Ru-Ru and heterometallic Ru-Os dimers and trimers were successfully synthesized by coordination to an π extended bipyridine-terpyridine bridge, and their electrochemical and photophysical characteristics were thoroughly investigated. The reduction processes of the heteronuclear complexes appear at more positive potentials compared with those of the mononuclear precursor complexes due to the strong stabilization of the π^* orbital of the coordinated terpyridine moieties. The trinuclear complexes show an absorption in the visible spectrum, and the molar coefficients of the ¹MLCT band (at ~517 nm, $\epsilon = 5.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) are higher than those of the precursor analogues ([Ru(bpy)₃]²⁺ at 451 nm, $\varepsilon = 1.1 \times$ $10^4 \text{ M}^{-1} \text{ cm}^{-1}$; [Ru(tpy)₂]²⁺ at 474 nm, $\epsilon = 1.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). These characteristics of the trinuclear complexes can be employed to develop functional materials for light absorption. Analysis of the luminescence properties showed that the potentially luminescent Ru-based bi- and trinuclear complexes do not exhibit any appreciable luminescence at room temperature (Table 2, Figure 3). The luminescence of the multinuclear complexes is weak, shifted to long wavelengths, and originates from the Ru-tpy motifs or Os-based centers. Thus, in each biand trinuclear complex, the excitation energy absorbed by the Ru-based moieties is quantitatively transferred to the combined Ru-tpy motif or Os-based unit. The short distance between energy donor (Ru-bpy) and acceptor (Ru-tpy) results in electron transfer rate constants of 3.9×10^6 s⁻¹ for **S–Ru–Ru** and $4.6 \times$ 10^6 s^{-1} for **D–Ru–Ru**. The luminescence spectra of the heteronuclear complexes S-Ru-Os (at 812 nm), D-Ru-Os (at 816 nm), and D-Os-Ru (at 833 nm) are in the near-infrared region (NIR). Relative to the polymeric Ru(II)-Os(II) species, the emission maximum is not in near-infrared region in spite of only a small number of polynuclear metal complexes are substantially redshifted to 790 nm.^[17a]

Experimental Section

Materials

4,4'-Dimethyl-2,2'-bipyridine and 2-acetylpyridine were purchased from Beijing Brilliant Technology Co., Ltd of China. Solvents and other raw materials of analytical grade were purchased from local commercial suppliers and used without further purification. The compounds 4-formyl-4'-methyl-2,2'-bipyridine,^[23] 4,4'-diformyl-2,2'bipyridine,^[24] 4,4'-ditpy-2,2'-bipyridine (L²),^[25] cis-[Ru-(bpy)₂Cl₂]-2H₂O,^[26] cis-[Os(bpy)₂Cl₂],^[27] Ru(tpy)Cl₃,^[28] and Os(tpy) Cl₃,^[29] have been prepared by previously reported procedures.



Instrumentation

¹H NMR spectra of all complexes were recorded on a Bruker AV III 400 MHz spectrometer using TMS as internal standard. HRMS (ESI) spectra were obtained on a Agilent 6224 mass spectrometer. IR spectra were recorded on a Thermo Nicolet AVATAR 360 FTIR spectrometer using KBr pellets. Spectroscopic spectra were recorded on a Varian Cary-100 UV/VIS spectrophotometer and Hitachi F-4600 instruments, and luminescence lifetime measurements were performed on a FLS 980 combined fluorescence-lifetime spectrometer. Electrochemical measurements were performed on a CHI 660D electrochemical workstation in MeCN or DMF under dinitrogen atmosphere.

Synthetic procedure

Synthesis of 4-tpy-4'-methyl-2,2'-bipyridine (L¹)

A solution of 4-formyl-4'-methyl-2.2'-bipyridine (0.50 g, 2.52 mmol) and NaOH (1.01 g, 25.2 mmol) in MeOH (100 mL) was stirred for 5 min at room temperature. Then, 2-acetylpyridine (0.80 mL, 5.56 mmol) was added, and the resulting mixed solution was continuously stirred for 3 h. Ammonium acetate (5.54 g, 72 mmol) was added, and the reaction mixture was heated to reflux overnight. The solution was cooled to room temperature and concentrated under reduced pressure. Subsequently, water (100 mL) was added, and the solution was extracted with CH₂Cl₂ (3×100 mL) and dried over Na₂SO₄. The organic layers were evaporated under vacuum to give the crude product, which was purified by chromatography on silica gel (ethyl acetate-hexanetriethylamine; 5:2:0.1, v/v) to obtain 4-tpy-4'-methyl-2,2'-bipyridine (0.52 g, 51%) as an off-white solid. ¹H NMR [400 MHz, CDCl₃, δ (ppm), J (Hz)]: 8.90 (d, 1H, 0.8), 8.86 (s, 2H), 8.83 (d, 1H, 4.8), 8.74 (dg, 2H, 0.8, 1.6), 8.70 (d, 2H, 8.0), 8.60 (d, 1H, 4.8), 8.31 (s, 1H), 7.90 (td, 1H, 1.6, 7.6), 7.80 (dd, 1H, 1.6, 4.8), 7.38 (ddd, 2H, 1.2, 4.8, 6.0), 7.18 (dd, 1H, 0.8, 4.8), 2.48 (s, 3H). ^{13}C NMR [400 MHz, CDCl₃, δ (ppm)]: 157.21, 156.34, 155.84, 155.61, 149.83, 149.20, 149.06, 148.25, 147.98, 147.24, 136.97, 125.01, 124.09, 122.19, 121.83, 121.42, 119.39, 119.02, 21.27. HRMS (ESI) in CH₂Cl₂ m/z calcd for [M +H]⁺: 402.1718; found: 402.1712. Anal. Calcd for C₂₆H₁₉N₅: C 77.79, H 4.77, N 17.44; found: C 77.70, H 4.71, N 17.39.

$[Ru(bpy)_{2}(\mu-L^{1})](PF_{6})_{2}(S-Ru)$

Cis-[Ru(bpy)₂Cl₂]·2H₂O (0.25 g, 0.48 mmol) and 4-tpy-4'-methyl-2,2'bipyridine (0.19 g, 0.48 mmol) were placed in 2-methoxyethanol (200 mL) and stirred at reflux for 5 h under nitrogen atmosphere, and the initial violet color changed to intense red. The reaction solution was cooled to room temperature and concentrated under reduced pressure to give the crude product, which was purified by chromatography on silica gel (elution with MeCN-saturated KNO₃-H₂O; 5:0.3:0.1, v/v). The eluent was evaporated under reduced pressure, the residue was dissolved in water, and the hexafluorophosphate salt of the complex was precipitated by the addition of saturated aqueous NH₄PF₆. The precipitate was filtered, washed with water, dissolved in a small amount of acetonitrile, and evaporated to dryness to obtain $[Ru(bpy)_2(\mu-L^1)](PF_6)_2$ (0.36 g, 67%) as an orange red solid. ¹H NMR [400 MHz, DMSO- d_{s} , δ (ppm), J (Hz)]: 9.33 (d, 1H, 1.2), 9.16 (s, 1H), 8.91-8.86 (m, 6H), 8.80 (d, 2H, 4.4), 8.73 (d, 2H, 7.6), 8.24-8.18 (m, 4H), 8.09 (td, 2H, 1.6, 7.6), 8.02 (dd, 1H, 1.6, 6.0), 7.90 (d, 1H, 5.6), 7.87 (d, 1H, 6.0), 7.82-7.76 (m, 3H), 7.64 (d, 1H, 6.0), 7.60–7.54 (m, 6H), 7.44 (d, 1H, 5.6), 2.58 (s, 3H). IR ν_{max} (KBr, cm⁻¹): 3435 (b), 1604 (w), 1583 (w), 1468 (m), 1446 (w), 1389 (w), 839 (s), 557 (s). HRMS (ESI) in MeCN m/z calcd for $[M-PF_6]^+$: 960.1690; found: 960.1711, *m/z* calcd for $[M-2(PF_6)]^{2+}$: 407.6024; found: 407.6038. Anal. Calcd for $C_{46}H_{35}N_9F_{12}P_2Ru$: C 50.01, H 3.19, N 11.41; found: C 49.97; H 3.17; N 11.42.

$[Os(bpy)_{2}(\mu-L^{1})](PF_{6})_{2}(S-Os)$

S–**Os** was synthesized from the precursors $Os(bpy)_2Cl_2$ (0.25 g, 0.44 mmol) and L¹ (0.18 g, 0.44 mmol) according to the same procedure as described above for **S**–**Ru** to obtain $[Os(bpy)_2(\mu-L^1)](PF_6)_2$ (0.34 g, 65%) as a black solid. ¹H NMR [400 MHz, DMSO- d_6 , δ (ppm), *J* (Hz)]: 9.31 (s, 1H), 9.14 (s, 1H), 8.89–8.85 (m, 6H), 8.79 (d, 2H, 4.4), 8.73 (d, 2H, 7.6), 8.10 (td, 2H, 1.6, 7.6), 8.04–7.97 (m, 4H), 7.91 (dd, 1H, 1.6, 6.0), 7.78 (t, 2H, 6.8), 7.71 (t, 2H, 6.4), 7.68 (d, 1H, 5.2), 7.60–7.57 (m, 2H), 7.54 (d, 1H, 6.0), 7.51–7.44 (m, 4H), 7.36 (d, 1H, 5.6), 2.67 (s, 3H). IR ν_{max} (KBr, cm⁻¹): 3435 (b), 1585 (w), 1463 (m), 1421 (w), 1389 (w), 1128 (w), 1026 (w), 841 (s), 762 (w), 557 (s). HRMS (ESI) in MeCN *m/z* calcd for [M–PF₆]⁺: 1050.2261; found: 1050.2254, *m/z* calcd for [M–2(PF₆)]²⁺: 452.6309; found: 452.6310. Anal. Calcd for $C_{46}H_{35}N_9F_{12}P_2Os$: C 46.30, H 2.91, N 10.47; found: C 46.37, H 2.89, N 10.40.

$[Ru(bpy)_2(\mu-L^1)Os(tpy)](PF_6)_4$ (S-Ru-Os)

 $[Ru(bpy)_{2}(\mu-L^{1})](PF_{6})_{2}$ (0.10 g, 0.090 mmol) and Os(tpy)Cl₃ (0.048 g, 0.090 mmol) were placed in ethylene glycol (50 mL) and stirred at reflux for 14 h under nitrogen atmosphere, and the initial red color changed to black. The reaction solution was cooled to room temperature and concentrated under reduced pressure to give the crude product, which was purified by chromatography on silica gel (elution with MeCN-saturated KNO3-H2O; 10:0.3:0.1, v/v). The eluent was evaporated under reduced pressure, the residue was dissolved in water, and the hexafluorophosphate salt of the complex was precipitated by the addition of saturated aqueous NH₄PF₆. The precipitate was filtered, washed with water, dissolved in a small amount of acetonitrile, and evaporated to dryness to obtain $[Ru(bpy)_2(\mu-L^1)Os(tpy)](PF_6)_4$ as a brown solid (0.074 g, 45%). ¹H NMR [400 MHz, DMSO-*d*₆, δ (ppm), *J* (Hz)]: 9.59 (s, 2H), 9.50 (s, 1H), 9.17 (d, 2H, 8.4), 9.03 (s, 1H), 9.00 (d, 2H, 8.4), 8.94 (d, 4H, 8.0), 8.87 (d, 2H, 8.4), 8.37 (d, 1H, 5.2), 8.24 (dd, 4H, 7.2, 14), 8.14 (t, 1H, 8.0), 8.02-7.99 (m, 3H), 7.93-7.89 (m, 3H), 7.85 (d, 3H, 5.2), 7.71 (d, 1H, 6.0), 7.61-7.58 (m, 4H), 7.53 (d, 1H, 5.6), 7.42 (d, 2H, 5.6), 7.31-7.26 (m, 4H), 7.18 (t, 2H, 6.8), 2.65 (s, 3H). IR ν_{max} (KBr, cm^{-1}): 3434 (b), 1620 (w), 1448 (w), 841 (s), 764 (w), 557 (s). HRMS (ESI) in MeCN m/z calcd for $[M-2(PF_6)]^{2+}$: 765.0944; found: 765.0936, m/zcalcd for [M-3(PF₆)]³⁺: 461.7417; found: 461.7408, m/z calcd for [M-4(PF₆)]⁴⁺: 310.0651; found: 310.0645. Anal. Calcd for C₆₁H₄₆N₁₂F₁₂P₄RuOs: C 40.29, H 2.55, N 9.24; found: C 40.20, H 2.41, N 9.27.

$[Os(bpy)_2(\mu-L^1)Ru(tpy)](PF_6)_4$ (S-Os-Ru)

S–Os–Ru was synthesized from the precursors $[Os(bpy)_2(\mu-L^1)](PF_6)_2$ (0.10 g, 0.084 mmol) and Ru(tpy)Cl₃ (0.037 g, 0.084 mmol) according to the same procedure as described above for **S–Ru–Os** to obtain $[Os(bpy)_2(\mu-L^1)Ru(tpy)](PF_6)_4$ as a greyish-green solid (0.072 g, 47%).¹H NMR [400 MHz, DMSO- d_6 , δ (ppm), *J* (Hz)]: 9.60 (s, 2H), 9.50 (s, 1H), 9.16 (d, 2H, 8.0), 9.01 (d, 3H, 7.2), 8.93–8.87 (m, 6H), 8.60 (t, 1H, 8.0), 8.26 (b, 1H, 5.2), 8.15 (t, 2H, 8.0), 8.06 (t, 6H, 7.6), 7.98 (d, 1H, 6.0), 7.82 (d, 1H, 5.6), 7.76 (d, 3H, 5.6), 7.62 (d, 1H, 5.6), 7.54–7.51 (m, 6H), 7.46 (d, 3H, 4.8), 7.34 (t, 2H, 6.4), 7.26 (t, 2H, 6.4), 2.74 (s, 3H). IR ν_{max} (KBr, cm⁻¹): 3433 (b), 1618 (w), 1466 (w), 1448 (w), 841 (s), 764 (w), 557 (s). HRMS (ESI) in MeCN *m/z* calcd for $[M-2(PF_6)]^{2+}$: 765.0944; found: 765.0938, *m/z* calcd for $[M-4(PF_6)]^{1+}$: 310.0651; found: 310.0645. Anal. Calcd for $C_{61}H_{46}N_{12}F_{24}P_4$ RuOs: C 40.29, H 2.55, N 9.24; found: C 40.20, H 2.41, N 9.27.



$[Ru(tpy)_2(\mu-L^1)Ru(tpy)](PF_6)_4$ (S-Ru-Ru)

S-**Ru**-**Ru** was synthesized from the precursors [Ru(bpy)₂(μ -L¹)](PF₆)₂ (0.10 g, 0.090 mmol) and Ru(tpy)Cl₃ (0.040 g, 0.090 mmol) according to the same procedure as described above for S-Ru-Os to obtain $[Ru(bpy)_2(\mu-L^1)Ru(tpy)](PF_6)_4$ as an orange-red solid (0.081 g, 52%). ¹H NMR [400 MHz, DMSO- d_{6} , δ (ppm), J (Hz)]: 9.60 (s, 2H), 9.53 (s, 1H), 9.16 (d, 2H, 8.0), 9.02-8.99 (m, 3H), 8.94 (d, 4H, 8.4), 8.89 (d, 2H, 8.4), 8.60 (t, 1H, 8.0), 8.38 (d, 1H, 6.0), 8.28-8.22 (m, 4H), 8.15 (t, 2H, 7.6), 8.08-8.04 (m, 3H), 7.93 (d, 1H, 6.0), 7.86 (d, 3H, 5.6), 7.72 (d, 1H, 6.0), 7.64-7.58 (m, 4H), 7.53 (d, 3H, 5.2), 7.46 (d, 2H, 5.6), 7.34 (t, 2H, 6.8), 7.26 (t, 2H, 6.8), 2.65 (s, 3H). IR ν_{max} (KBr, cm^{-1}): 3435 (b), 1585 (w), 1466 (w), 1448 (w), 841 (s), 762 (w), 557 (s). HRMS (ESI) in MeCN *m*/*z* calcd for [M–PF₆]⁺: 1585.0959; found: 1585.0996, *m*/*z* calcd for [M-2(PF₆)]²⁺: 720.0659; found: 720.0673, m/z calcd for [M-4(PF₆)]⁴⁺: 287.5508; found: 287.5512. Anal. Calcd for $C_{61}H_{46}N_{12}F_{24}P_4Ru_2$: C 42.37, H 2.68, N 9.72; found: C 42.25, H 2.71, N 9.62.

$[Ru(bpy)_{2}(\mu-L^{2})](PF_{6})_{2}(D-Ru)$

D–**Ru** was synthesized from the precursors L² (0.24 g, 0.38 mmol), *cis*-[Ru(bpy)₂Cl₂] · 2H₂O (0.20 mg, 0.38 mmol), and ethylene glycol (100 mL) according to the same procedure as described above for **S**–**Ru** to obtain [Ru(bpy)₂(μ -L²)](PF₆)₂ as a red solid (0.31 g, 60%). ¹H NMR [400 MHz, DMSO-*d*₆, δ (ppm), *J* (Hz)]: 9.69 (d, 2H, 1.6), 8.93 (d, 4H, 8.0), 8.89 (s, 4H), 8.77–8.76 (m, 4H), 8.73 (d, 4H, 8.0), 8.27–8.22 (m, 4H), 8.10–8.04 (m, 6H), 7.96–7.92 (m, 4H), 7.83 (d, 2H, 5.2), 7.63–7.56 (m, 8H). IR v_{max} (KBr, cm⁻¹): 3435 (b), 1583 (w), 1468 (w), 1390 (w), 841 (s), 557 (s). HRMS (ESI) in MeCN *m/z* calcd for [M–PF₆]⁺: 1177.2330; found: 1177.2398, *m/z* calcd for [M–2(PF₆)]²⁺: 516.1344; found: 516.1353. Anal. Calcd for C₆₀H₄₂N₁₂F₁₂P₂Ru: C 54.51, H 3.20, N 12.71; found: C 54.44, H 3.24, N 12.60.

$[Os(bpy)_{2}(\mu-L^{2})](PF_{6})_{2}(D-Os)$

D–**Os** was synthesized from the precursors *cis*- $[Os(bpy)_2Cl_2]$ (0.20 g, 0.35 mmol), L² (0.22 g, 0.35 mmol), and ethylene glycol (100 mL) according to the same procedure as described above for **S**–**Ru** to obtain $[Os(bpy)_2(\mu-L^2)](PF_6)_2$ as a black solid (0.21 g, 57%). ¹H NMR [400 MHz, DMSO- d_6 , δ (ppm), *J* (Hz)]: 9.69 (d, 2H, 1.6), 8.91 (dd, 4H, 3.6, 8.0), 8.89 (s, 4H), 8.77–8.76 (m, 4H), 8.73 (d, 4H, 7.6), 8.10–8.08 (m, 4H), 8.06–8.03 (m, 4H), 7.94 (dd, 2H, 2.0, 6.0), 7.86 (d, 4H, 6.0), 7.73 (d, 2H, 5.6), 7.59–7.57 (m, 4H), 7.56–7.54 (m, 2H), 7.53–7.50 (m, 2H). IR v_{max} (KBr, cm⁻¹): 3435 (b), 1585 (w), 1468 (w), 1390 (w), 843 (s), 557 (s). HRMS (ESI) in MeCN *m/z* calcd for $[M-PF_6]^+$: 1267.2901; found: 1267.2898, *m/z* calcd for $[M-2(PF_6)]^{2+}$: 561.1629; found: 561.1634. Anal. Calcd for $C_{60}H_{42}N_{12}F_{12}P_2Os$: C 51.07, H 3.00, N 11.91; found: C 51.19, H 2.91, N 11.96.

$[Ru(bpy)_{2}(\mu-L^{2})(Os(tpy))_{2}](PF_{6})_{6} (D-Ru-Os)$

 $(NH_4)_2OsCl_6$ (0.060 g, 0.14 mmol) and 2,2':6',2''-terpyridine (0.032 g, 0.14 mmol) were placed in ethylene glycol (50 mL) and stirred under reflux for 8 h under nitrogen atmosphere. The solution was cooled to room temperature, $[Ru(bpy)_2(\mu-L^2)](PF_6)_2$ (0.090 g, 0.070 mmol) was added, and reflux was continued for 10 h under nitrogen atmosphere. The solution was again cooled to room temperature and concentrated under reduced pressure to give the crude product, which was purified by chromatography on silica gel (elution with MeCN-saturated KNO₃-H₂O; 10:0.5:0.2, v/v). The eluent was evaporated under reduced pressure, the residue was dissolved in water, and the hexafluorophosphate salt of the complex was precipitated by the addition of saturated aqueous NH_4PF_6 . The precipitate was filtered, washed with water, dissolved

in a small amount of acetonitrile, and evaporated to dryness to obtain $[Ru(bpy)_2(\mu-L^2)(Os(tpy))_2](PF_6)_6$ as a purple solid (0.074 g, 45 %). ¹H NMR [400 MHz, DMSO- d_6 , δ (ppm), J (Hz)]: 9.88 (s, 2H), 9.74 (s, 4H), 9.18 (d, 4H, 8.0), 9.07–9.00 (m, 8H), 8.86 (d, 4H, 8.4), 8.59 (d, 2H, 5.6), 8.32 (dd, 4H, 6.8, 14), 8.16–8.12 (m, 4H), 8.05 (d, 2H, 5.6), 8.01–7.97 (m, 6H), 7.90 (t, 4H, 7.6), 7.70 (d, 4H, 2.0), 7.44 (d, 4H, 5.2), 7.31–7.25 (m, 8H), 7.16 (t, 4H, 6.4). IR ν_{max} (KBr, cm⁻¹): 3435 (b), 1620 (w), 1605 (w), 1450 (w), 1385 (w), 1028 (w), 843 (s), 764 (m), 557 (s). HRMS (ESI) in MeCN *m/z* calcd for $[M-2PF_6]^{2+}$: 1231.1184; found: 1231.1182, *m/z* calcd for $[M-3(PF_6)]^{3+}$: 772.4242; found: 772.4240, *m/z* calcd for $[M-4(PF_6)]^{4+}$: 543.0771; found: 543.0768, *m/z* calcd for $[M-6(PF_6)]^{2+}$: 313.7300; found: 313.7296. Anal. Calcd for $C_{90}H_{64}N_{18}F_{36}P_6Os_2Ru: C 39.32, H 2.35, N 9.17;$ found: C 39.21, H 2.38, N 9.11.

$[Os(bpy)_{2}(\mu-L^{2})(Ru(tpy))_{2}](PF_{6})_{6}(D-Os-Ru)$

 $[Os(bpy)_2(\mu-L^2)](PF_6)_2$ (0.070 g, 0.05 mmol) and RuCl₃·3H₂O (0.021 g, 0.10 mmol) were placed in ethylene glycol (50 mL) and refluxed for 8 h under nitrogen atmosphere. The solution was cooled to room temperature, 2,2':6',2"-terpyridine (0.024 g, 0.10 mmol) was added, and reflux was continued for 10 h under nitrogen atmosphere. The solution was again cooled to room temperature and concentrated under reduced pressure to give the crude product, which was purified by chromatography on silica gel (elution with MeCNsaturated KNO₂-H₂O; 10:0.5:0.2, v/v). The eluent was evaporated under reduced pressure, the residue was dissolved in water, and the hexafluorophosphate salt of the complex was precipitated by the addition of saturated aqueous NH₄PF₆. The precipitate was filtered, washed with water, dissolved in a small amount of acetonitrile, and evaporated to dryness to obtain $[Os(bpy)_2(\mu -$ L²)(Ru(tpy))₂](PF₆)₆ as a gray solid (0.067 g, 51%). ¹H NMR [400 MHz, DMSO-d₆, δ (ppm), J (Hz)]: 9.90 (s, 2H), 9.75 (s, 4H), 9.15 (d, 4H, 8.0), 9.10 (d, 4H, 8.0), 9.01 (t, 4H, 7.2), 8.88 (d, 4H, 8.4), 8.60 (t, 2H, 8.0), 8.48 (d, 2H, 5.6), 8.17-8.09 (m, 10H), 8.04 (t, 4H, 7.6), 7.93 (d, 2H, 5.6), 7.89 (d, 2H, 5.2), 7.60 (dd, 4H, 7.6, 14), 7.53 (d, 4H, 5.2), 7.45 (d, 4H, 5.6), 7.32 (t, 4H, 6.4), 7.23 (t, 4H, 6.4). IR ν_{max} (KBr, cm^{-1}): 3479 (b), 3415 (b), 1618 (w), 1450 (w), 843 (s), 766 (w), 557 (s). HRMS (ESI) in MeCN m/z calcd for [M-3(PF₆)]³⁺: 742.4052; found: 742.4075, m/z calcd for [M-4(PF₆)]⁴⁺: 520.5628; found: 520.5648, m/z calcd for [M-5(PF₆)]⁵⁺: 387.4574; found: 387.4587, *m/z* calcd for [M-6(PF₆)]²⁺: 298.7205; found: 298.7210. Anal. Calcd for C₀₀H₆₄N₁₈F₃₆P₆OsRu₂: C 40.64, H 2.43, N 9.48; found: C 40.65, H 2.35, N 9.36.

$[Ru(bpy)_{2}(\mu-L^{2})(Ru(tpy))_{2}](PF_{6})_{6} (D-Ru-Ru)$

D-Ru-Ru was synthesized from the precursors $[Ru(bpy)_2(\mu-L^2)](PF_6)_2$ (0.070 g, 0.053 mmol), RuCl₃·3H₂O (0.022 g, 0.11 mmol), and 2,2':6',2"-terpyridine (0.025 g, 0.11 mmol) according to the same procedure as described above for D-Os-Ru to obtain [Ru(bpy)₂(µ- L^{2} (Ru(tpy))₂] (PF₆)₆ as an orange-red solid (0.060 g, 51%). ¹H NMR [400 MHz, DMSO-d₆, δ (ppm), J (Hz)]: 9.94 (s, 2H, 2H₃), 9.76 (s, 4H, $2H_{3''} + 2H_{5''}$), 9.14 (d, 4H, 8.4, $2H_{11} + 2H_{13}$), 9.09 (d, 4H, 7.6, $2H_{3'} + 2H_{13}$) $2H_{3''}$), 9.01 (d, 4H, 5.6, $2H_d + 2H_e$), 8.87 (d, 4H, 8.0, $2H_{10} + 2H_{14}$), 8.61(d, 4H, 7.6, 2H₅+2H₁₂), 8.32 (dd, 4H, 6.8, 13.2, 2H_c+2H_f), 8.17 (d, 2H, 6.0, 2H₆), 8.11 (t, 4H, 7.6, $2H_{a'} + 2H_{a'''}$), 8.06 (d, 6H, 7.2, $2H_9 + 2H_{15}$ $+2H_{a(h)}$), 7.99 (d, 2H, 5.2, 2H_{a(h)}), 7.68 (dd, 4H, 5.6, 12, 2H_h + 2H_n), 7.52 (d, 4H, 5.2, $2H_{6'} + 2H_{6''}$), 7.44 (d, 4H, 5.2, $2H_7 + 2H_{17}$), 7.32 (t, 4H, 6.4, $2H_{5'} + 2H_{5''}$), 7.23 (t, 4H, 6.4, $2H_8 + 2H_{16}$). IR v_{max} (KBr, cm⁻¹): 3435 (b), 1618 (w), 843 (s), 764 (w), 557 (w). HRMS (ESI) in MeCN m/z calcd for [M-2(PF₆)]²⁺: 1141.0613; found: 1141.0651, *m/z* calcd for [M-4(PF₆)]⁴⁺: 498.0486; found: 520.0500, *m*/*z* calcd for [M-5(PF₆)]⁵⁺: 369.4460; found: 369.4471, *m/z* calcd for [M–6(PF₆)]²⁺: 283.7110;



found: 283.7120. Anal. Calcd for $C_{\rm 90}H_{64}N_{18}F_{36}P_6Ru_3:$ C 42.05, H 2.51, N 9.81; found: C 42.13, H 2.40, N 9.66.

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Conflict of Interest

The authors declare no conflict of interest.

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