Synthesis and properties of an efficient and switchable photosensitizing unit, [Ru(4,4′-diphenyl-2,2′-bipyridine)₂-(7-amino-dipyrido[3,2-a:2′,3′-c]phenazine)]²⁺, for a photo-induced energy transfer system †

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A Ru(II) complex containing the 4,4′-diphenyl-2,2′-bipyridine (Ph_2bpy) and 7-amino-dipyrido[3,2-a:2′,3′-c]-phenazine (dppz-NH_2) ligands was synthesized and found to be an excellent switchable photosensitizing unit suitable for photo-induced energy transfer, which has large light absorptivity, superior excited state properties and an amino functional unit for connecting acceptor units. [Os(tpy)₂]²⁺ (tpy = 2,2′:6′,2″-terpyridine) unit was connected to the amino group of this photosensitizing unit by an amide bond to construct a heterodinuclear Ru(II)/Os(II) photo-induced energy transfer system. This system showed stronger Os(II) centered emission compared to the similar heterodinuclear Ru(II)/Os(II) complex containing 2,2′-bipy (bpy) instead of Ph_2bpy. Analysis of the photophysical processes of these complexes indicated that the stronger Os(II) emission was ascribed not only to the higher absorptivity but also to the increased energy transfer efficiency from the Ru(II) to the Os(II) center. It also demonstrated that photosensitization by energy transfer to the Os(II) center was switched on and off reversibly by protonation/deprotonation of the dppz moiety.

Introduction

Construction of efficient photo-induced energy transfer systems has been the subject of intense studies because of their important role in various rapidly developing fields like artificial solar energy harvesting systems,[1] molecular-level devices for nanoscale electronics,[2,3] and sophisticated molecular sensors.[4] The system is composed of photosensitizing, connecting and acceptor units, and various connecting units for efficient and long-distance energy transfer have been reported.[5] However, the type of photosensitizing units used for these studies is relatively limited. Porphyrins,[6] organic laser dyes[7] and polypyridyl Ru(II) complexes[8] are the most frequently used for this purpose. Development of useful photosensitizing units is one of the key factors for construction of photo-induced energy transfer systems. The criteria for a photosensitizing unit are that the unit has (i) large light absorptivity for effective light harvesting or high sensitivity for input light, (ii) superior excited state properties to increase the efficiency of energy transfer to the acceptor unit, and (iii) suitable functional group(s) for connecting the acceptor unit. To meet the requirements of (i), dendron-type photosensitizing units have been reported.[6a,7,8c,9]

We previously synthesized [Ru(bpy)₂(dppz-NH_2)]²⁺ (dppz-NH_2 = 7-amino-dipyrido[3,2-a:2′,3′-c]phenazine) having an amino terminal group as a useful photosensitizing and connecting unit for energy transfer systems, and showed that efficient intramolecular energy transfer took place from the Ru(II) center to the energy-accepting unit connected to the amino terminal group by the amide bond.[10]

In 1984, Cook *et al.* reported the synthesis and emission properties of [Ru(Ph_2bpy)$_{3−n}$(bpy)$_n$][PF₆]₂ (Ph_2bpy = 4,4′-diphenyl-2,2′-bipyridine, n = 0, 1 and 2).[11] These complexes showed high radiative quantum yields of 0.306, 0.098 and 0.197 for n = 0, 1 and 2, respectively, which was ascribed to the

delocalization of the excited electron to the phenyl groups.[12] In spite of these excellent emission properties, to the best of our knowledge, an energy transfer system using this [Ru(Ph_2-bpy)₃]²⁺ unit as the photosensitizing chromophore has not been reported. Therefore, in this study, [Ru(Ph_2bpy)₂(dppz-NH_2)]²⁺ was synthesized as a novel photosensitizing unit that satisfy the above-mentioned criteria, possessing excellent light harvesting ability and high emission properties compared to Ru-bpy systems, and an amino terminal group for connecting acceptor units. An [Os(tpy)₂]²⁺ unit, which has a higher radiative quantum yield than [Os(bpy)₃]²⁺, was introduced to the amino group of this photosensitizing unit, and intramolecular energy transfer within this heterodinuclear Ru(II)/Os(II) complex was examined. We will demonstrate here that [Ru(Ph_2bpy)₂(dppz-NH_2)]²⁺ is an excellent building block as the efficient and switchable photosensitizing unit for construction of a photo-induced energy transfer system.

Results

Synthesis

The reaction scheme is illustrated in Fig. 1. The parent complex, [Ru(Ph_2bpy)₂(dppz-NH_2)]²⁺ (**Ru(Ph)-NH₂**), used as a photosensitizing unit, was easily synthesized in moderate yield (67%) from Ru(Ph_2bpy)₂Cl₂ and dppz-NH_2[13] by a one-step reaction. The parent complex was reacted with tpy-Ph-COCl, prepared by acid chlorination of tpy-Ph-COOH,[14] to give [Ru(Ph_2bpy)₂(dppz-NHCO-Ph-tpy)]²⁺. Although TLC showed the presence of some impurities at this stage, subsequent reaction with [Os(tpy)(H₂O)₃]³⁺[15] and purification by preparative TLC yielded a Ru(II)/Os(II) heterodinuclear complex, **Ru(Ph)-NHCO-Os** as a dense brown powder. The heterodinuclear complex containing bpy instead of Ph_2bpy, **Ru-NHCO-Os**, was synthesized by the same procedure. The reference complex having no Os(II) center, **Ru(Ph)-NHCO**, was obtained by preparation of the amide bridging ligand dppz-NHCO-Ph-Buᵗ and subsequent complexation with Ru(Ph_2bpy)₂Cl₂, and **Ru-NHCO**
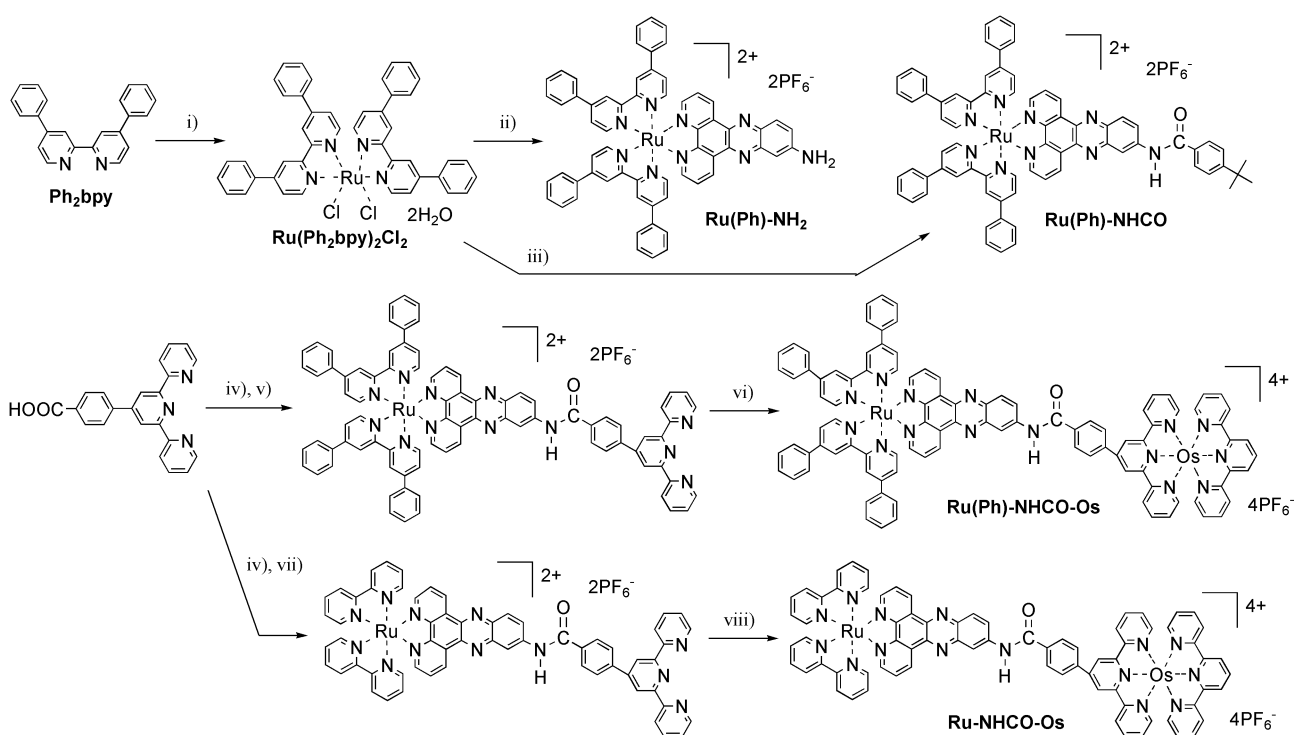
Fig. 1 Synthetic scheme of the complexes. (i) RuCl₃ hydrate, LiCl–dmf, reflux for 8 h; (ii) 7-dppz-NH₂–2-methoxyethanol, reflux for 5 h; (iii) dppz-NHCO-Ph-Buᵗ–EtOH, H₂O, reflux for 5 h; (iv) SOCl₂, reflux for 6 h; (v) **Ru(Ph)-NH₂**–*N*,*N*-dimethylacetamide (DMAc), pyridine, 120 °C for 37 h, then NH₄PF₆; (vi) [Os(tpy)(H₂O)₃][PF₆]₃–ethylene glycol, 150 °C for 1 h; (vii) [Ru(bpy)₂(dppz-NH₂)][PF₆]₂–DMAc, pyridine, 120 °C for 37 h, then NH₄PF₆; (viii) [Os(tpy)(H₂O)₃][PF₆]₃–ethylene glycol, 150 °C for 3 h.

was prepared according to the literature.[10] Each complex could be purified by preparative TLC on silica with acetonitrile–0.4 M aqueous KNO₃ or ammonium hexafluorophosphate–acetonitrile solution as an eluent. The purity of the complexes was carefully confirmed by TLC, and all new compounds were characterized by ¹H NMR spectroscopy and FAB or ES mass spectrometry.

Absorption and emission spectra of the complexes

The absorption spectra of the mononuclear and heterodinuclear complexes (1.00×10^{-5} M) were measured in acetonitrile at 25 °C, which are shown in Fig. 2a and 2b, respectively, together with their emission spectra, and the data are collected in Table 1. The high-intensity absorption band at about 300 nm can be ascribed to the ligand-centered π–π* transition.[10] A broad band between 350 and 500 nm consists of both the ligand-centered π–π*/n–π* absorption band of the dppz-NH₂ ligand and the spin-allowed metal-to-ligand charge transfer (¹MLCT) band. For the heterodinuclear complexes, **Ru-NHCO-Os** and **Ru(Ph)-NHCO-Os**, the spin-forbidden MLCT (³MLCT) band appeared between 550 and 750 nm.

The emission spectra of the complexes (1.00×10^{-6} M) were measured by excitation at 440 nm. Emission from the Ru(II) center appeared at 620–630 nm, while emission from the Os(II) center was observed at 746 nm. To enhance the comparison, intensities of the emission from the Ru(II) and the Os(II) centers were reported as relative to those of **Ru-NHCO** and **Ru-NHCO-Os**, respectively. In Table 1, the emission intensities were described in the form of both those under the same concentration and those normalized by the absorbance at 440 nm (in proportion to the emission quantum yield), respectively. Though **Ru(Ph)-NH₂** having an amine end group showed relatively weak emission, **Ru(Ph)-NHCO** having an amide end group showed about 4.97 times stronger emission than **Ru-NHCO**. Using [Ru(bpy)₃]²⁺ ($\phi = 0.062$ in acetonitrile[16]) as a reference, the emission quantum yield of **Ru(Ph)-NHCO** was estimated to be 0.10.
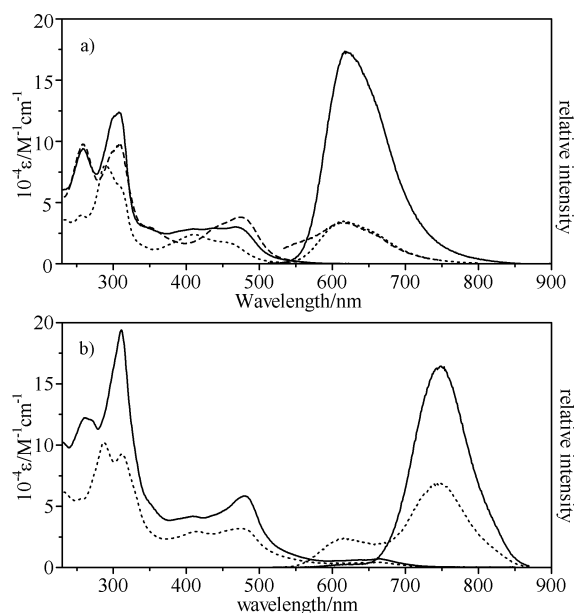
Fig. 2 Absorption (left hand) and emission (right hand) spectra of (a) mononuclear and (b) heterodinuclear complexes in acetonitrile at 25 °C. λ_{ex} = 440 nm; (a) **Ru(Ph)-NH₂** (---), **Ru-NHCO** (· · ·), **Ru(Ph)-NHCO** (—), (b) **Ru-NHCO-Os** (· · ·), **Ru(Ph)-NHCO-Os** (—). Emission intensity is magnified 10 times in (b) compared to that in (a).

In **Ru(Ph)-NHCO-Os**, the emission from the Ru(II) center was completely quenched, suggesting that the intramolecular energy transfer took place from the Ru(II) center to the Os(II) center.

Lifetime measurements

In order to clarify the energy transfer process in the heterodinuclear **Ru(Ph)-NHCO-Os**, the time-resolved emission decay curves of **Ru(Ph)-NHCO-Os**, **Ru-NHCO-Os** and reference complexes were recorded at an approximate concentration of

Table 1 Absorption and emission properties at 25 °C

Complex	Absorption λ_{max}/nm ($10^{-4}\varepsilon$/cm^{-1} M^{-1})					Emission λ_{max}/nm, rel. int. (rel. int./abs.)[a]		Emission lifetime τ/ns	
						Ru based	Os based	Ru based	Os based
Ru(Ph)-NH$_2$	260 (9.77)	309 (9.87)	474 (3.81)			611, 0.97 (0.63)			
Ru(Ph)-NHCO	259 (9.40)	308 (12.38)	410 (2.86)	467 (3.02)		621, 4.97 (3.23)		873	
Ru(Ph)-NHCO-Os	262 (12.23)	311 (19.39)	408 (4.19)	480 (5.85)	665 (0.71)	621, 0.006 (0.004)	746, 2.40 (1.54)	15	182
Ru-NHCO	257 (3.98)	290 (8.04)	412 (2.40)	460 (1.71)		615, ≡1.00 (≡1.00)		138	
Ru-NHCO-Os	287 (10.22)	312 (9.30)	414 (2.94)	475 (3.19)	661 (0.43)	621, 0.081 (0.068)	746, ≡1.00 (≡1.00)	14	166

[a] The parentheses show the relative values of the emission intensity divided by the absorbance at 440 nm.

Table 2 Redox potentials (V *vs.* Fc/Fc$^+$)

	Reductions				Os$^{3+/2+}$	Ru$^{3+/2+}$
Ru(Ph)-NH$_2$	$[-2.06]^a$	$[-1.67]^b$	$[-1.50]^b$	$[-1.23]^a$		0.88
Ru(Ph)-NHCO	$[-1.90]^a$	-1.72	-1.36			0.85
Ru(Ph)-NHCO-Os	$[-1.75]^a$	$[-1.59]^b$	$[-1.49]^b$	$[-1.31]^a$	0.52	0.85
Ru-NHCO^c	-1.86	-1.45				0.85
[Ru(Ph$_2$bpy)$_3$]$^{2+\,d}$		-1.66				0.82

[a] Peak potential of the reduction wave. [b] Peak potential of the oxidation wave. [c] Ref. 10. [d] Ref. 12a.

10^{-4} M in acetonitrile. Emission at 620 nm of the reference complexes, **Ru(Ph)-NHCO** and **Ru-NHCO**, showed single exponential decay curves with lifetime of 873 and 138 ns, respectively. In the case of **Ru(Ph)-NHCO-Os**, decay curves at 620 nm (Ru(II) center) and 740 nm (Os(II) center) fitted to the single decay process, giving 15 and 182 ns as the lifetimes, respectively. Based on the emission lifetimes from the Ru(II) centers of **Ru(Ph)-NHCO** (τ^0) and **Ru(Ph)-NHCO-Os** (τ), the rate of energy transfer (k_{en}) was estimated to be 6.6×10^7 s^{-1} ($k_{en} = (1/\tau) - (1/\tau^0)$). Similarly, emission decay curves of **Ru-NHCO-Os** at 620 nm (Ru(II) center) and 740 nm (Os(II) center) fitted to the single decay process, giving 14 and 166 ns as the lifetimes, respectively, and the rate of energy transfer in the **Ru-NHCO-Os** complex was estimated to be 6.4×10^7 s^{-1}. It is noted that the emission from the Os(II) center in the time-resolved emission decay curves of **Ru(Ph)-NHCO-Os** and **Ru-NHCO-Os** showed risetime at the initial stage, which roughly coincided with the rapid decay of the emission from the Ru(II) center (see Electronic Supplementary Information†).

Electrochemistry

Cyclic voltammetry of the complexes in acetonitrile was carried out in the range between +1.41 to −2.09 V *vs.* Fc/Fc$^+$, and the potentials are summarized in Table 2. In the positive region, the complexes exhibited reversible one-electron redox peaks due to a Ru^{2+}/Ru^{3+} couple at +0.85–+0.88 V *vs.* Fc/Fc$^+$ and/or reversible one-electron redox peaks due to a Os^{2+}/Os^{3+} couple at 0.52 V *vs.* Fc/Fc$^+$. The peak intensities of the Os^{2+}/Os^{3+} and Ru^{2+}/Ru^{3+} couples in the heterodinuclear complexes were identical, indicating that there was no internal metal–metal interaction between two metal centers.

In the negative region, **Ru(Ph)-NHCO** exhibited reversible first reduction couples at −1.36 V due to the reduction of the phenazine unit[10] and reversible second reduction couples at −1.72 V *vs.* Fc/Fc$^+$ which is ascribed to the reduction of the Ph$_2$bpy ligand.[12a] In the case of the other complexes, the voltammograms became less well-defined or irreversible, and only the peak potentials of the reduction or the oxidation waves are listed.

Protonation/deprotonation of the dppz moiety

It is known that [Ru(L)$_2$(dppz)]$^{2+}$ (L = bpy or 1,10-phenanthroline) showed moderate emission in acetonitrile and ethanol, but no emission in water or in the presence of a proton donor such as acetic acid.[17] This was ascribed to the protonation of the dppz nitrogen, which caused effective dissipation of the dppz-localized MLCT excited state. This result prompted us to test the switching of the photo-induced energy transfer from the Ru(II) to the Os(II) center by protonation/deprotonation of the dppz moiety in **Ru(Ph)-NHCO-Os**. First, the absorption and emission spectral changes of **Ru(Ph)-NHCO** (4.0×10^{-6} M) by adding CF$_3$SO$_3$H (2.0×10^{-2} M, 5000 equivalent) and subsequently Et$_3$N (5000 equivalent) in acetonitrile were measured. Upon addition of acid, the MLCT band was slightly red-shifted and the emission from the Ru(II) center was greatly decreased (1/50) as shown in Fig. 3a. The absorption and emission spectra returned to the original shape again following addition of base, and these spectral changes, induced by the protonation/deprotonation cycle, could be repeated reversibly. Next, the absorption and emission spectral changes of **Ru(Ph)-NHCO-Os** (4.0×10^{-6} M) were measured. Addition of acid (2.0×10^{-2} M, 5000 equivalent) caused a red-shift of the MLCT band and concomitant decrease of the emission from the Os(II) center (1/5) as shown in Fig. 3b. Since addition of acid little affected the emission intensity of the Os(II) center by irradiation at 665 nm, where no absorption due to the Ru(II) center was observed, the acid-induced decrease of the Os(II) emission was due to the switching off of the photosensitization by the Ru(II) unit. The absorption and emission spectra recovered the original shape again on addition of base (5000 equivalent), and these spectral changes were confirmed to be reversible.

Discussion

Photophysical properties of photosensitizing unit, Ru(Ph)-NHCO

It is clearly shown in Fig. 2 that the complexes containing the Ph$_2$bpy ligand have a more than 1.5 times larger extinction coefficient throughout the UV-VIS region than those containing
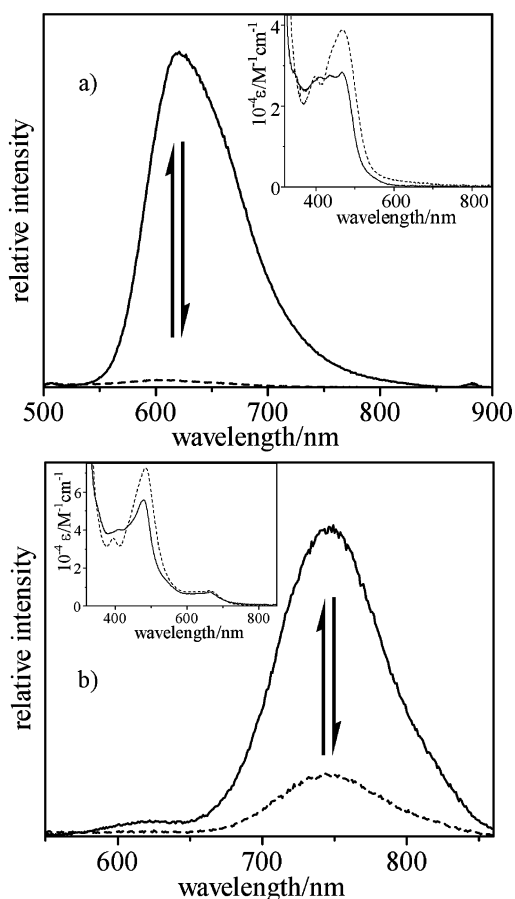
Fig. 3 Emission spectral changes of (a) **Ru(Ph)-NHCO** and (b) **Ru(Ph)-NHCO-Os** by protonation/deprotonation in acetonitrile at 25 °C. $\lambda_{ex} = 440$ nm; protonated form (- - -), deprotonated form (—). Each inset shows the corresponding absorption spectral change. Emission intensity is magnified 5 times in (b) compared to that in (a).

the bpy ligand. The increase of the absorptivity of the π–π* band can be attributed to the presence of additional phenyl groups in Ph_2bpy, but it is worth noting that the MLCT band at 360–420 nm was also increased. A similar increase of the MLCT band was also observed for [Ru(4,4′-di-*p*-tolyl-bpy)$_3$]$^{2+}$.[12a] These results demonstrated that Ru(II) complexes containing the Ph_2bpy ligand serve as superior light harvesting units compared to those containing the bpy ligand.

The concentration-based emission intensity of **Ru(Ph)-NHCO** by excitation at 440 nm is 4.97 times stronger than that of **Ru-NHCO** (Table 1). This increase is attributed in part to the increased absorbance of **Ru(Ph)-NHCO** at 440 nm. However, the emission intensity of **Ru(Ph)-NHCO** normalized by the absorbance is still 3.23 times higher than that of **Ru-NHCO**. This should be due to the superior emission properties of **Ru(Ph)-NHCO**. From the emission lifetimes, rates of dissipation from the emission states were estimated to be 1.15×10^6 s^{-1} and 7.25×10^6 s^{-1} for **Ru(Ph)-NHCO** and **Ru-NHCO**, respectively, showing clearly that the dissipation of the excited energy in **Ru(Ph)-NHCO** is much slower than that in **Ru-NHCO**. Thus, it is shown that an Ru(II) complex containing the Ph_2bpy ligand has excellent light harvesting abilities and superior excited state properties, suitable as a photosensitizing unit for constructing a photo-induced energy transfer system.

Energy transfer process from the photosensitizing unit

The emission intensity from the Os(II) center of **Ru(Ph)-NHCO-Os** by excitation at 440 nm is 2.4 times stronger than that of **Ru-NHCO-Os** in the same concentration (Table 1).[18] The emission intensity of **Ru(Ph)-NHCO-Os** after being normalized by absorbance is still 1.54 times higher, indicating a

higher emission efficiency of **Ru(Ph)-NHCO-Os**. To understand this result, the absorption process is examined more in detail. Since the Os(II) center itself has an absorption at 440 nm, direct excitation of the Os(II) center also contributes to the emission from the Os(II) center. From the absorbance of the MLCT band of [Os(tpy)$_2$]$^{2+}$ at 440 nm ($\varepsilon = 7900$ cm^{-1} M^{-1}), absorption by the Os(II) center was estimated to comprise 18 and 28% of the total absorption at 440 nm for **Ru(Ph)-NHCO-Os** and **Ru-NHCO-Os**, respectively. Therefore, a major part of the light excitation within these complexes is the Ru(II) center, and the proportion of the Ru(II) excitation is higher for **Ru(Ph)-NHCO-Os**. These results clearly showed that the higher emission efficiency of **Ru(Ph)-NHCO-Os** is ascribed to the higher energy transfer efficiency from the Ru(II) to the Os(II) center within the complex, demonstrating that the **Ru(Ph)-NHCO** serves as an efficient photosensitizing unit.

To enhance comparison, rates of photophysical processes within the heterodinuclear complexes are summarized in Fig. 4. Though the rate of energy transfer was practically identical for these complexes, the rate of dissipation of the excited energy at the Ru(II) center was much faster in **Ru-NHCO-Os**. The rate of the energy transfer was only less than an order of magnitude faster in this case, and therefore, the excited energy dissipation at the Ru(II) center might reduce the efficiency of the energy transfer process. In contrast, the rate of energy transfer is more than 50 times faster than that of dissipation at the Ru(II) center in **Ru(Ph)-NHCO-Os**. Therefore, this can be the reason, at least in part, for the higher efficiency of the energy transfer process in **Ru(Ph)-NHCO-Os**. Energy transfer for longer distances or through non-conjugated structures generally resulted in a smaller rate, and, therefore, this factor should become more important for construction of efficient energy transfer systems.
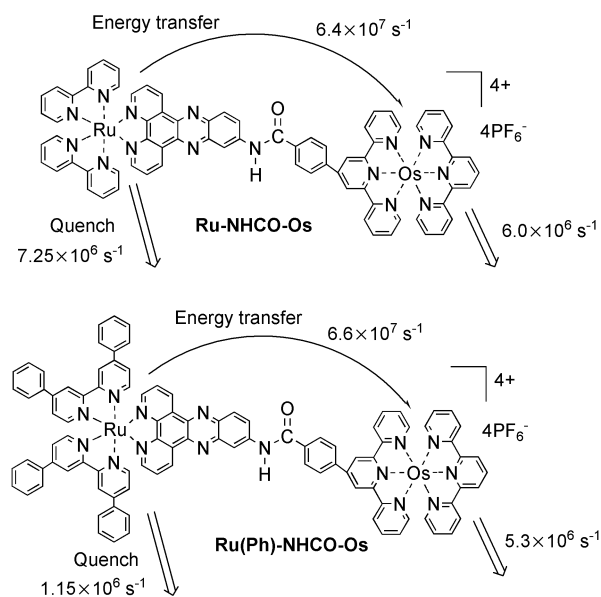
Fig. 4 Rates of photophysical processes in **Ru-NHCO-Os** and **Ru(Ph)-NHCO-Os**.

Switching of the energy transfer process from the photosensitizing unit

It has been reported that protonation of the [Ru(bpy)$_2$(dppz)]$^{2+}$ complex occurred at the phenazine nitrogen which caused quenching of the emission.[17] As shown in Fig. 3a, it is clearly noted that the emission from the Ru(II) center of **Ru(Ph)-NHCO** could be reversibly switched on and off by protonation/deprotonation. In the case of **Ru(Ph)-NHCO-Os**, addition of acid decreased the emission from the Os(II) center to 20% of the original intensity (Fig. 3b). The remaining emission is presumably due to the direct excitation of the Os(II) center, which nearly corresponds to the absorbance ratio of the Os(II) center
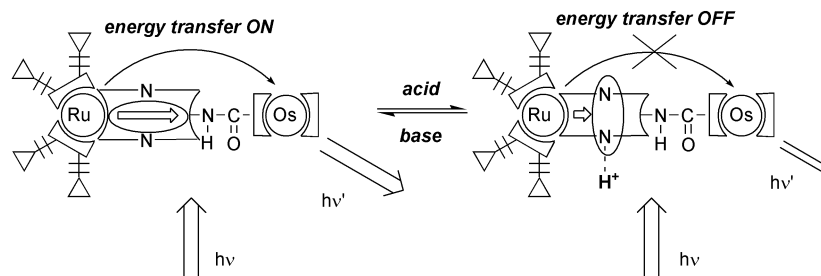
Fig. 5 Illustration of energy transfer switching by protonation/deprotonation in **Ru(Ph)-NHCO-Os**.

at 440 nm (18%, see above). Since protonation of the dppz unit caused a large increase of the dissipation process at the Ru(II) center,[17] the result is explained by switching off of the photosensitizing ability of the Ru(II) unit within the complex. The scheme of energy transfer switching by protonation/deprotonation in **Ru(Ph)-NHCO-Os** is illustrated in Fig. 5. The process is fully reversible by addition of acid and base alternately, and the change of the emission intensity is sufficiently large to be easily monitored. Therefore, **Ru(Ph)-NHCO** serves not only as an efficient but also a switchable photosensitizing unit by protonation/deprotonation of the dppz moiety.

Conclusion

We showed that the Ru(II) complex, **Ru(Ph)-NHCO**, containing the Ph_2bpy and dppz-NH_2 ligands, is an excellent photosensitizing unit having (i) large light absorptivity for effective light harvesting or high sensitivity for input light, (ii) superior excited state properties to increase the efficiency of energy transfer to the acceptor unit, and (iii) an amino functional group suitable for connecting the acceptor units, and demonstrated the importance of the above factors by preparation and examining the photophysical properties of **Ru(Ph)-NHCO-Os**. The photosensitizing ability of this unit can be switched on and off reversibly by protonation/deprotonation of the dppz moiety, which is another advantage of this photosensitizing unit. Since a variety of acceptor units can be connected to this unit simply by an amide bond, **Ru(Ph)-NHCO** can be a useful and excellent building block for construction of energy transfer systems.

Experimental

General method

Solvents and reagents were of reagent grade quality and used as received unless otherwise specified. 7-dppz-NH_2,[13] [Ru(bpy)$_2$-(dppz-NH_2)][PF$_6$]$_2$,[10] [Ru(bpy)$_2$(dppz-NHCO-Ph-Bu^t)][PF$_6$]$_2$ (**Ru-NHCO**),[10] [Os(tpy)$_2$]$^{2+}$ [19] and [Os(tpy)(H$_2$O)$_3$][PF$_6$]$_3$[15] were prepared according to the literature procedures. Tpy-Ph-COOH was prepared according to the literature procedure,[14] but by an improved method using CH_3OH as the crystallized solvent instead of dmso (the yield was increased from 18 to 25%). The ^1H NMR spectra were recorded on a JEOL JNM-LA400 spectrometer in $CDCl_3$ or CD_3CN. Mass spectra were recorded on a JEOL JMS-600H spectrometer equipped with MS-ESIP09 for ES-MS. Absorption and emission spectra were measured with a Shimadzu UV-2500PC spectrophotometer and Shimadzu RF-5300PC spectrofluorophotometer, respectively. Cyclic voltammetry was conducted in N_2-Purged CH_3CN containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte with a BAS Electrochemical Analyser Model 720 A. A glassy carbon or a platinum disk was used as the working electrode, a Ag/Ag$^+$ electrode as the reference and a Pt wire as the counter electrode. All redox waves were referenced to internal ferrocene added at the end of each experiment. Redox potentials are quoted *vs.* the ferrocene/ferrocenium couple (Fc/Fc$^+$ = 0.0 V). The time-resolved emission decay was measured by irradiation of sample solutions in N_2-Purged CH_3CN with a nitrogen laser pulse (Hamamatsu Photonics LN120C2, 337 nm) through a coumarin chromophore (447 nm). The emission was then dispersed with a Hamamatsu Photonics C-2830 disperser and monitored on Hamamatsu Photonics M-2548 streak camera.

Synthesis

$Ru(Ph_2bpy)_2Cl_2 \cdot 2H_2O$

A mixture of 4,4′-Ph_2bpy (297 mg, 0.963 mmol), ruthenium(III) chloride hydrate (126 mg, 0.482 mmol) and LiCl (139 mg, 3.20 mmol) in dmf (5 mL) was refluxed for 8 h. The reaction mixture was cooled to room temperature. Acetone (25 mL) was added to this solution, which was placed in the refrigerator overnight. The resulting precipitate was filtered on a glass filter, washed with H_2O and diethyl ether, and dried *in vacuo* to yield a black–purple powder (355 mg, 90%). FAB-MS m/z = 788 [M], 753 [M−Cl]$^+$.

$[Ru(Ph_2bpy)_2(dppz-NH_2)][PF_6]_2$ (Ru(Ph)-NH$_2$)

A mixture of $Ru(Ph_2bpy)_2Cl_2$ (86 mg, 0.104 mmol) and 7-dppz-NH_2 (33 mg, 0.111 mmol) in 2-methoxyethanol (36 mL) was refluxed for 5 h. The reaction mixture was cooled to room temperature, to which excess aqueous NH_4PF_6 (400 mg) was added. The precipitate was collected by filtration on celite, washed with water and diethyl ether, and re-dissolved with CH_3CN. The filtrate was evaporated and the residue was dried *in vacuo* to give a reddish–black powder (136 mg). The crude product was purified by preparative TLC on silica with CH_3CN–0.4 M aqueous KNO_3 (10:1) as eluent to give a reddish–orange powder (88 mg, 67%). R_f (silica) = 0.43: CH_3CN : 0.4 M aqueous KNO_3 = 9 : 1; Mp > 375 °C; ^1H NMR (400 MHz, CD_3CN, 20 °C): δ = 9.63 (dd, J = 8.3, 1.2 Hz, 1H), 9.56 (dd, J = 8.3, 1.2 Hz, 1H), 9.00 (d, J = 1.7 Hz, 2H), 8.96 (d, J = 1.7 Hz, 2H), 8.28 (dd, J = 5.4, 1.2 Hz, 1H), 8.22 (dd, J = 5.4, 1.5 Hz, 1H), 8.16 (d, J = 9.0 Hz, 1H), 8.02 (dd, J = 6.2, 1.2 Hz, 2H), 7.98 (dd, J = 7.8, 1.2 Hz, 4H), 7.88–7.90 (m, 6H), 7.80 (dd, J = 6.1, 1.5 Hz, 2H), 7.76 (dd, J = 6.1, 1.5 Hz, 2H), 7.55–7.65 (m, 15H), 7.29 (d, J = 2.7 Hz, 1H), 5.53 (br s, 2H); FAB-MS m/z = 1160 [M−PF$_6$]$^+$, 1015 [M−2PF$_6$]$^+$, 507.6 [M−2PF$_6$]$^{2+}$.

$[Ru(Ph_2bpy)_2(dppz-NHCO-Ph-Bu^t)][PF_6]_2$ (Ru(Ph)-NHCO)

A mixture of dppz-NHCO-Ph-Bu^t (51 mg, 0.111 mmol) and $Ru(Ph_2bpy)_2Cl_2$ (90 mg, 0.109 mmol) in de-aerated EtOH–H_2O (1:1, 24 mL) was refluxed for 5 h. The reaction mixture was cooled to room temperature. EtOH was evaporated from the solution, to which excess aqueous NH_4PF_6 (400 mg) was added. The precipitate was collected by filtration on celite, washed with water and diethyl ether, and re-dissolved with CH_3CN. The filtrate was evaporated and the residue was dried *in vacuo* to give a reddish–orange powder (106 mg). The crude product was purified by column chromatography on silica with CH_3CN–0.4 M aqueous KNO_3 (9:1) as eluent followed by crystallization from ethanol to yield a reddish–orange powder (65 mg, 40%). R_f (silica) = 0.46: CH_3CN : 0.4 M aqueous KNO_3 = 9 : 1; Mp >

375 °C; ^{1}H NMR (400 MHz, CD$_3$CN, 20 °C): δ = 9.45 (d, J = 8.3 Hz, 1H), 9.42 (d, J = 8.3 Hz, 1H), 9.29 (s, 1H), 9.03 (d, J = 1.7 Hz, 2H), 8.99 (d, J = 1.7 Hz, 2H), 8.72 (s, 1H), 8.35 (d, J = 5.4 Hz, 1H), 8.28 (d, J = 5.4 Hz, 1H), 8.17 (d, J = 9.0 Hz, 1H), 8.07 (d, J = 5.9 Hz, 2H), 8.01 (d, J = 7.1 Hz, 2H), 7.99 (d, J = 7.6 Hz, 2H), 7.96 (d, J = 6.1 Hz, 1H), 7.80–7.92 (m, 11H), 7.54–7.67 (m, 17H), 1.35 (s, 9H); FAB-MS m/z = 1320 [M−PF$_6$]$^+$, 1176 [M−2PF$_6$]$^+$, 589 [M−2PF$_6$]$^{2+}$.

[Ru(Ph$_2$bpy)$_2$(dppz-NHCO-Ph-tpy)][PF$_6$]$_2$

Tpy-Ph-COOH (31 mg, 0.0714 mmol) was refluxed in SOCl$_2$ (2 mL) for 6 h. Excess SOCl$_2$ was removed *in vacuo* to give the acid chloride which was used directly without characterization in the next step. A solution of **Ru(Ph)-NH$_2$** (79 mg, 0.0605 mmol) in *N,N*-dimethylacetamide (2.5 mL) was added to a solution of the acid chloride in pyridine (1 mL), and the resulting solution was stirred at 120 °C for 37 h. The reaction mixture was cooled to room temperature, to which excess aqueous NH$_4$PF$_6$ (492 mg) was added. The precipitate was collected by filtration on celite, washed with water and diethyl ether, and re-dissolved with CH$_3$CN. The filtrate was evaporated and the residue was dried *in vacuo* to give a orange powder (91 mg, 91%). Although TLC showed the presence of some impurities, we used this product for the next reaction. ES-MS m/z = 1495 [M−PF$_6$]$^+$, 675 [M−2PF$_6$]$^{2+}$.

[Ru(Ph$_2$bpy)$_2$(dppz-NHCO-Ph-tpy)Os(tpy)][PF$_6$]$_4$ (Ru(Ph)-NHCO-Os)

A solution of [Ru(Ph$_2$bpy)$_2$(dppz-NHCO-Ph-tpy)][PF$_6$]$_2$ (72 mg, 0.0439 mmol) and [Os(tpy)(H$_2$O)$_3$][PF$_6$]$_3$ (41 mg, 0.0449 mmol) in ethylene glycol (13 mL) was stirred at 150 °C for 1 h. The reaction mixture was cooled to room temperature, to which excess aqueous NH$_4$PF$_6$ (302 mg) was added. The precipitate was collected by filtration on celite, washed with water and diethyl ether, and re-dissolved with CH$_3$CN. The filtrate was evaporated and the residue was dried *in vacuo* to give a dense brown powder (94 mg). The crude product was purified by preparative TLC on silica with CH$_3$CN–0.4 M aqueous KNO$_3$ (3:1) and then with CH$_3$CN–0.4 M aqueous KNO$_3$ (5:1) and finally with NH$_4$PF$_6$ (4 mg)–acetonitrile (1 mL) as eluent to give a dense brown powder (5.5 mg, 5%). R_f (silica) = 0.45: CH$_3$CN : 0.4 M aqueous KNO$_3$ = 5 : 1; 0.41: NH$_4$PF$_6$ (4 mg)–CH$_3$CN (1 mL); Mp > 375 °C; ^{1}H NMR (400 MHz, CD$_3$CN, 20 °C): δ = 9.79 (dd, J = 8.3, 1.2 Hz, 1H), 9.70 (dd, J = 8.3, 1.2 Hz, 1H), 9.68 (s, 1H), 9.21 (d, 2.2 Hz, 1H), 9.10 (s, 2H), 9.02 (d, J = 1.7 Hz, 2H), 8.98 (d, J = 1.7 Hz, 2H), 8.78 (d, J = 8.3 Hz, 2H), 8.66 (d, J = 8.3 Hz, 2H), 8.53 (d, J = 8.3 Hz, 1H), 8.49 (d, J = 8.3 Hz, 2H), 8.33–8.45 (m, 7H), 8.05 (d, J = 5.9 Hz, 2H), 7.94–8.00 (m, 6H), 7.91 (dd, J = 7.8, 1.2 Hz, 4H), 7.78–7.86 (m, 9H), 7.58–7.67 (m, 14H), 7.30 (d, J = 6.1 Hz, 2H), 7.26 (d, J = 6.1 Hz, 2H), 7.10–7.14 (overlapping d (2H) and d (2H), J = 6.1 Hz); ES-MS m/z = 2208 [M−PF$_6$]$^+$, 1032 [M−2PF$_6$]$^{2+}$.

[Ru(bpy)$_2$(dppz-NHCO-Ph-tpy)][PF$_6$]$_2$

Tpy-Ph-COOH (77 mg, 0.149 mmol) was refluxed in SOCl$_2$ (3 mL) for 6 h. Excess SOCl$_2$ was removed *in vacuo* to give the acid chloride which was used directly without characterization in the next step. A solution of [Ru(bpy)$_2$(dppz-NH$_2$)][PF$_6$]$_2$ (100 mg, 0.0999 mmol) in *N,N*-dimethylacetamide (1 mL) was added to a solution of the acid chloride in pyridine (1.5 mL) and *N,N*-dimethylacetamide (1.5 mL), and the resulting solution was stirred at 120 °C for 37 h. The reaction mixture was cooled to room temperature, to which excess aqueous NH$_4$PF$_6$ (500 mg) was added. The precipitate was collected by filtration on celite, washed with water and diethyl ether, and re-dissolved with CH$_3$CN. The filtrate was evaporated and the residue was dried *in vacuo* to give a orange powder (110 mg, 82%). Although TLC showed the presence of some impurities, we

used this product for the next reaction. FAB-MS m/z = 1191 [M−PF$_6$]$^+$, 1046 [M−2PF$_6$]$^+$.

[Ru(bpy)$_2$(dppz-NHCO-Ph-tpy)Os(tpy)][PF$_6$]$_4$ (Ru-NHCO-Os)

A solution of [Ru(bpy)$_2$(dppz-NHCO-Ph-tpy)][PF$_6$]$_2$ (65 mg, 0.0487 mmol) and [Os(tpy)(H$_2$O)$_3$][PF$_6$]$_3$ (44 mg, 0.0482 mmol) in ethylene glycol (15 mL) was stirred at 150 °C for 3 h. The reaction mixture was cooled to room temperature, to which excess aqueous NH$_4$PF$_6$ (200 mg) was added. The precipitate was collected by filtration on celite, washed with water and diethyl ether, and re-dissolved with CH$_3$CN. The filtrate was evaporated and the residue was dried *in vacuo* to give a dense brown powder (83 mg). The crude product was purified by preparative TLC on silica with CH$_3$CN–0.4 M aqueous KNO$_3$ (3:1) and then with NH$_4$PF$_6$ (8 mg)–CH$_3$CN (1 mL) and finally with CH$_3$CN–0.4 M aqueous KNO$_3$ (3:1) as eluent to give a dense brown powder (3.5 mg, 3.5%). R_f (silica) = 0.23: CH$_3$CN : 0.4 M aqueous KNO$_3$ = 5 : 1; 0.37: NH$_4$PF$_6$ (8 mg)–CH$_3$CN (1 mL); Mp > 375 °C; ^{1}H NMR (400 MHz, CD$_3$CN, 20 °C): δ = 9.80 (s, 1H), 9.75 (dd, J = 8.3, 1.2 Hz, 1H), 9.66 (dd, J = 8.3, 1.2 Hz, 1H), 9.21 (d, 2.2 Hz, 1H), 9.11 (s, 2H), 8.78 (d, J = 8.3 Hz, 2H), 8.67 (d, J = 8.3 Hz, 2H), 8.57 (d, J = 8.3 Hz, 2H), 8.54 (d, J = 8.3 Hz, 2H), 8.49 (d, J = 8.3 Hz, 2H), 8.45 (d, J = 8.3 Hz, 2H), 8.39 (d, J = 8.3 Hz, 2H), 8.18 (dt, J = 5.4, 1.2 Hz, 2H), 8.13 (dt, J = 8.3, 1.2 Hz, 2H), 8.04 (t, J = 8.3 Hz, 2H), 7.96 (t, J = 8.3 Hz, 1H), 7.86–7.93 (m, 6H), 7.84 (dd, J = 7.6, 1.5 Hz, 2H), 7.80 (dd, J = 7.8, 1.2 Hz, 2H), 7.75–7.77 (m, 4H), 7.48 (t, J = 6.7 Hz, 2H), 7.25–7.31 (m, 6H), 7.12 (dt, J = 6.1, 1.2 Hz, 4H); ES-MS m/z = 1904 [M−PF$_6$]$^+$, 880.4 [M−2PF$_6$]$^{2+}$.

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