$[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ Complex ($dppz\text{-}NH_2$: 7-Amino-dipyrido[3,2-*a* : 2′,3′-*c*]phenazine) as a Useful Photosensitizing Unit for the Construction of Photoinduced Energy Transfer Systems

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7-Amino-dipyrido[3,2-*a* : 2′,3′-*c*]phenazine ($dppz\text{-}NH_2$) has a diimine coordination site, a rigid and extended π conjugation system, and a reactive amino group within the molecule, and $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ was synthesized as a useful photosensitizing unit for the construction of photoinduced energy-transfer systems. Anthraquinone, anthracene, and $[Os(bpy)_3]^{2+}$ derivatives having a carboxylic acid function were used as energy-accepting units, and were successfully connected to $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ through an amide bond. Electronic spectral and electrochemical studies of the resultant complexes were carried out, and it was shown that effective excited electron or energy transfer took place from the Ru(II) polypyridyl center to these units. In the case of the heterodinuclear Ru(II)/Os(II) complex, emission from the Ru(II) polypyridyl center was effectively quenched and that from the Os(II) polypyridyl center was increased compared to the reference Os(II) polyimine complex. The rate of energy transfer from the Ru(II) to the Os(II) polypyridyl center through the dppz-amide connector was estimated to be 1.0×10^8 s^{-1} in acetonitrile.

The development of molecular and supramolecular systems showing efficient photoinduced energy or electron transfer[1] are of current research interest due to their applications in various chemical and biological processes.[2] In this context, Ru(II) polyimine complexes have been extensively exploited as an ideal component of systems suitable for such investigations, owing to their outstanding excited state[3] and redox properties.[4] Ruthenium(II) complex having dppz (dipyrido[3,2-*a* : 2′,3′-*c*]phenazine) as a ligand was first reported by Ackermann and Interrante.[5] Since the dppz unit has a rigid and extended π-conjugation system, $[RuL_2(dppz)]^{2+}$ (L: 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen)) complexes have been used as a DNA intercalation agent.[6] Bridging ligands having the dppz structural unit as a part of rigid conjugation systems have also been reported.[7]

In our studies on fluorescent polypyridyl compounds,[8] we found that 7-amino-dppz ($dppz\text{-}NH_2$) shows relatively strong fluorescence, presumably from the phenazine-localized excited state.[9] The excitation spectrum of 7-amino-dppz showed an efficient internal conversion from the bipyridine-localized to the phenazine-localized excited state. Relatively strong fluorescence of 7-amino-dppz assured that the phenazine-localized excited state is less vulnerable to the radiationless deactivation process. Since the compound has a diimine-type metal chelating site and a reactive amino group, it can be employed as a useful building block in a photoinduced energy/electron-transfer system between diimine-coordinated metal center and the functional unit(s) attached to the amino group. Therefore, in this study, $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ was synthesized as a novel photosensitizing unit suitable for constructing photoinduced energy transfer systems, and anthraquinone and other energy-accepting units were connected to the amino group of this photosensitizing unit by an amide bond.

The photophysical and electrochemical properties of these Ru(II) complexes were studied and discussed in view of the photoinduced energy or electron transfer within the complex. In particular, a heterodinuclear Ru(II)/Os(II) complex having an Os(II) bipyridyl unit as the energy-accepting unit was studied as an efficient intramolecular photoinduced energy transfer system from the Ru(II) to the Os(II) center.

Results

Syntheses and Structures of the Complexes. The parent complex, $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$, used as a photosensitizing unit, was easily prepared in high yield (86%) from $[RuCl_2(bpy)_2]$ and 7-amino-dppz by a one-step reaction. This parent complex could be purified through a Sephadex LH-20 column by acetonitrile as an eluent. The parent complex was reacted with various acid chlorides to give the target complexes.

The synthesized complexes are listed in Fig. 1: $[RuAT]^{2+}$, $[RuAC]^{2+}$, $[RuAPQ]^{2+}$, $[RuAQ]^{2+}$, $[RuAA]^{2+}$, $[RuAB]^{2+}$, and heterodinuclear Ru(II)/Os(II) complex $[RuABOs]^{4+}$. A mononuclear Os(II) complex, $[Os(bpy)_2(bdbpa)]^{2+}$ (bdbpa: 2,2′-bipyridine-4,4′-di(4-*t*-butylphenylamide)) was also synthesized as a reference complex. Alternatively, $[RuAT]^{2+}$ was obtained by preparing a bridging ligand 7-(4-*t*-butylbenzoylamino)-dppz and undergoing subsequent complexation with $[RuCl_2(bpy)_2]$. These complexes could be pu-

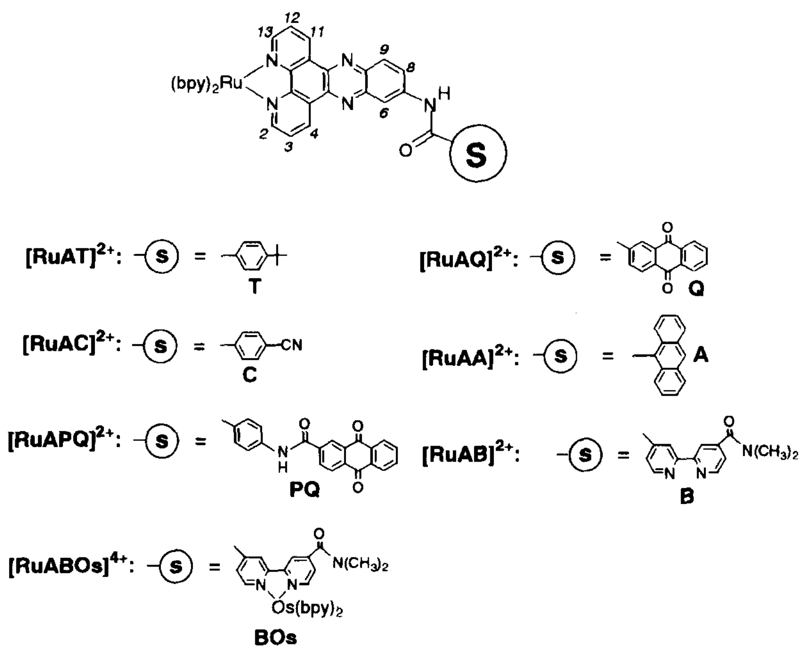

Fig. 1. Ru(II) complexes synthesized from $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$.

rified through the best selection of an alumina column or alumina/silica preparative TLC with ammonium hexafluorophosphate/acetonitrile solution as an eluent.

Complexes obtained as PF_6 salts were orange to brown powders, and attempts to crystallize them from various solvents were unsuccessful. All of the complexes were characterized by ^{1}H NMR (^{1}H-^{1}H COSY) and mass spectrometry, as well as elemental analyses. Since the structures of the complexes are similar to each other, their structures were successfully interpreted from their ^{1}H NMR spectra.

Absorption Spectra of the Complexes. The absorption spectra of the complexes (1.00×10^{-5} mol dm^{-3}) were measured in acetonitrile at 25 °C, and are shown in Figs. 2, 3, and 4 together with their emission spectra. A broad band between 350 and 500 nm was composed of both the ligand-centered π–π*/n–π* absorption band of the 7-amino-dppz ligand[9] and the spin-allowed metal-to-ligand charge transfer (MLCT) band from the Ru(II) center to the diimine ligands.[10] The ligand-centered π–π* transition was also observed at about 300 nm.[9] In the case of heterodinuclear $[RuABOs]^{4+}$, the spin-forbidden MLCT band from the Os(II) center to diimine ligands appeared between 550 and 800 nm.[10]

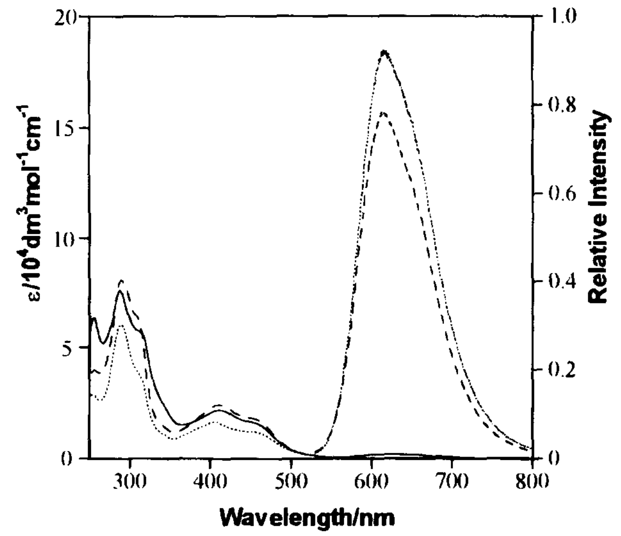

Fig. 2. Absorption and emission spectra of Ru(II) complexes in acetonitrile at 25 °C; $[RuAT]^{2+}$ (- - -), $[RuAC]^{2+}$ (····), and $[RuAPQ]^{2+}$ (—).

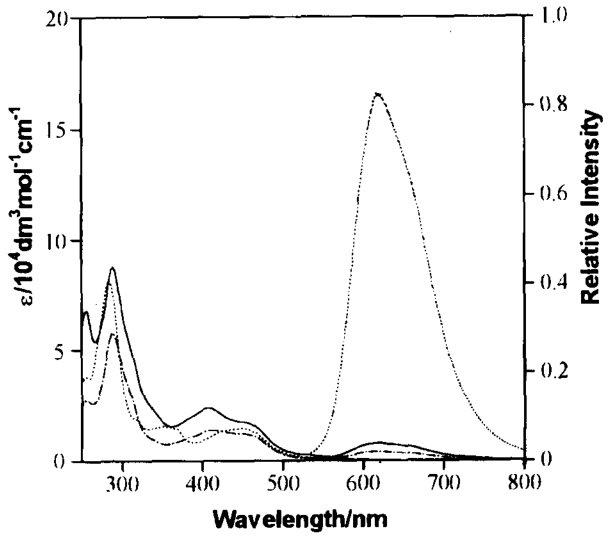

Fig. 3. Absorption and emission spectra of Ru(II) complexes in acetonitrile at 25 °C; $[RuAQ]^{2+}$ (—), $[RuAA]^{2+}$ (– • –), and $[Ru(bpy)_2(dppz)]^{2+}$ (····).

The absorption spectral data of these complexes are summarized in Table 1 together with their emission spectral data. The spin-allowed MLCT bands of these complexes are not much different from each other, even with those of $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$, $[Ru(bpy)_2(dppz)]^{2+}$, and $[Ru(bpy)_3]^{2+}$ appearing at around 440—450 nm. Therefore, the acid com-

Table 1. Absorption and Emission Data of Ru(II) Complexes in Acetonitrile at 25 °C

Complexes	Absorption λ_{max}/nm ($\varepsilon/10^4$ dm^3 mol^{-1} cm^{-1})						Emission λ_{max}/nm (intensity)[a]	
7-Amino-dppz[b]	438	304^{sh}	290	240			534	
	(0.97)	(3.03)	(3.14)	(2.86)				
$[Ru(bpy)_2(dppz)]^{2+}$	448	354	318^{sh}	285	256		620	
	(1.44)	(1.55)	(1.85)	(8.07)	(3.79)		(0.82)	
$[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$	468	318	288	257			610	
	(2.50)	(4.46)	(7.26)	(4.57)			(0.03)	
$[RuAT]^{2+}$	460^{sh}	412	310^{sh}	290	257		615	
	(1.71)	(2.40)	(6.28)	(8.04)	(3.98)		(0.78)	
$[RuAC]^{2+}$	458^{sh}	407	316^{sh}	289	254		615	
	(1.17)	(1.63)	(3.47)	(6.05)	(2.86)		(0.92)	
$[RuAPQ]^{2+}$	460^{sh}	412	314^{sh}	288	255		614	
	(1.54)	(2.17)	(5.68)	(7.58)	(6.35)		(0.01)	
$[RuAQ]^{2+}$	458^{sh}	407	288	256			620	
	(1.68)	(2.39)	(8.76)	(6.78)			(0.04)	
$[RuAA]^{2+}$	460^{sh}	413	289	255			610	
	(1.14)	(1.37)	(5.78)	(2.74)			(0.02)	
$[RuAB]^{2+}$	458^{sh}	406	289	255	236		620	
	(1.80)	(2.42)	(9.82)	(4.79)	(4.79)		(0.57)	
$[RuABOs]^{4+}$	681[c]	505^{sh}	446	407	289	253	620	732[d]
	(0.36)	(2.53)	(3.76)	(3.81)	(16.15)	(7.14)	(0.005)	(1.76)

a) Intensities are relative to that of $[Ru(bpy)_3]^{2+}$ (1.00×10^{-6} mol dm^{-3}) in aqueous solution at λ_{ex} = 440 nm. b) See the Ref. 9 partly. c) Broad. d) Intensity is relative to that of $[Os(bpy)_2(bdbpa)]^{2+}$ (1.00×10^{-6} mol dm^{-3}) in acetonitrile at λ_{ex} = 440 nm.

ponents connected through the amide bond showed little effect on the MLCT excited state of the Ru(II) polyimine center.

Emission Spectra of the Complexes. The emission spectra of the complexes (1.00×10^{-6} mol dm^{-3}) by excitation at 440 nm were measured in acetonitrile at 25 °C, which are also shown in Figs. 2, 3, and 4; the data are summarized in Table 1. The emission intensities of the Ru(II) complexes were normalized by the absorbance at 440 nm, and were reported as relative to that of $[Ru(bpy)_3]^{2+}$. In the case of the heterodinuclear $[RuABOs]^{4+}$, the emission intensity from the Ru(II) center was reported relative to that of $[Ru(bpy)_3]^{2+}$, while that from the Os(II) center was normalized by the absorbance at 440 nm and was reported relative to that of $[Os(bpy)_2(bdbpa)]^{2+}$.

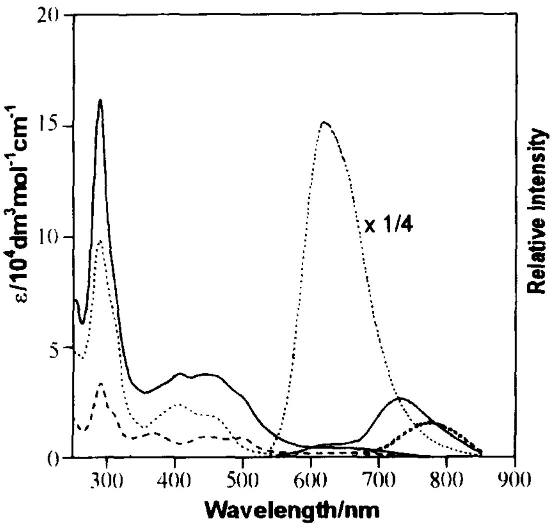

Fig. 4. Absorption and emission spectra of Ru(II)/Os(II) complexes in acetonitrile at 25 °C; $[RuAB]^{2+}$ (····), $[RuABOs]^{4+}$ (—), and $[Os(bpy)_2(bdbpa)]^{2+}$ (- - -).

The emission band of the Ru(II) complexes appeared at 610—620 nm, and little difference was observed between each other, including $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_2(dppz)]^{2+}$, and the parent complex $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$. Since the fluorescence of 7-amino-dppz appeared at 534 nm,[9] the observed emission was not from the attached energy-accepting unit nor 7-amino-dppz, but mostly from the Ru(II) polyimine center. However, their intensities were different. $[Ru(bpy)_2(dppz)]^{2+}$ showed moderate emission, but $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ showed only a very weak emission. Mononuclear $[RuAT]^{2+}$ or $[RuAC]^{2+}$ having *t*-butylphenyl or cyanophenyl unit, respectively, showed relatively strong emission, similar to that of $[Ru(bpy)_3]^{2+}$.

However, when anthraquinone was attached to the parent complex through the amide bond, $[RuAQ]^{2+}$, the emission from the Ru(II) center was almost totally quenched. Moreover, $[RuAPQ]^{2+}$, having an anthraquinone unit at the 4-position of the benzoylamide group, showed only a very weak emission. $[RuAA]^{2+}$, having anthracene, also showed almost no emission.

In the case of complexes having a bipyridyl unit, $[RuAB]^{2+}$ showed moderate emission (relative intensity 0.57). However, the emission from the Ru(II) center of heterodinuclear $[RuABOs]^{4+}$ was almost quenched (0.005), though that from the Os(II) center increased by 1.7 times stronger compared to that of the reference complex, $[Os(bpy)_2(bdbpa)]^{2+}$. The results suggested intramolecular energy transfer from the Ru-

(II) center to the Os(II) center.

Life Time Measurement of Heterodinuclear $[RuABOs]^{4+}$ Complex. In order to clarify the energy-transfer process in the heterodinuclear $[RuABOs]^{4+}$, further, the time-resolved emission decay curves of $[RuABOs]^{4+}$ were recorded together with those of reference complexes, $[RuAB]^{2+}$ and $[Os(bpy)_2(bdbpa)]^{2+}$, in the concentration range of 1×10^{-2}—1×10^{-3} M in acetonitrile. Emission decay curves of the reference complexes, $[RuAB]^{2+}$ at 600 nm and $[Os(bpy)_2(bdbpa)]^{2+}$ at 730 nm, showed single exponential decay curves with lifetimes (τ) of 128 and 35 ns, respectively. In the case of the heterodinuclear $[RuABOs]^{4+}$, decay curves at 600 (Ru center) and 730 nm (Os center) fitted to the single decay process, giving 9 and 30 ns as the lifetimes, respectively.

Electrochemical Properties of Ru(II) Complexes. Cyclic voltammetry of the complexes (5.00×10^{-4} mol dm^{-3}) in acetonitrile was carried out in the range between +1.47 to −1.75 V vs. SCE at 25 °C; the results are summarized in Table 2. In the positive region, all of the complexes showed reversible one-electron redox peaks due to a Ru^{2+}/Ru^{3+} couple at +1.25—+1.27 V vs. SCE;[1e] also, no other redox peaks were observed up to 1.47 V vs. SCE. In the case of heterodinuclear $[RuABOs]^{4+}$, reversible redox peaks due to an Os^{2+}/Os^{3+} couple appeared at +0.83 V vs. SCE[1e] in addition to peaks due to the Ru^{2+}/Ru^{3+} couple at +1.25 V vs. SCE. Since the peak intensities of the Os^{2+}/Os^{3+} and Ru^{2+}/Ru^{3+} couples were identical, there was no direct metal–metal interaction electrochemically in the heterodinuclear $[RuABOs]^{4+}$.

In the negative region, $[Ru(bpy)_2(dppz)]^{2+}$ showed reversible first reduction couples at −1.00 V vs. SCE (Table 2), which are in good agreement with the reported potential (−1.02 V vs. SCE),[11] and have been ascribed to reduction of the phenazine unit.[11] Similar reversible first reduction couples were observed for $[RuAT]^{2+}$, $[RuAC]^{2+}$, and $[RuAA]^{2+}$, but $[RuAB]^{2+}$ and $[RuABOs]^{4+}$ showed irreversible waves with only the reduction wave. Below the first reduction couple, the voltammogram became less well-defined and complicated. Therefore, we list the reduction potentials down to −1.5 V vs. SCE in Table 2 and discussed only the first reduction couples. These reduction potentials were not much different from each other or from that of $[Ru(bpy)_2(dppz)]^{2+}$ in spite of the structural difference of their acid components attached through the amide bond. Therefore, the first reduction potentials of these complexes are due to the reduction of the dppz moiety.[11] However, in the case of $[RuAQ]^{2+}$ and $[RuAPQ]^{2+}$, two successive reduction waves were observed between −0.83—−1.10 V vs. SCE, but oxidation waves were not well separated especially in the case of $[RuAQ]^{2+}$. Therefore, only the peak potentials of the reduction waves are listed in Table 2. Since anthraquinone derivatives bearing amide-substituents at 2-position have high electron affinity showing their reduction potentials in the range between −0.79—−0.83 V vs. SCE,[12,13] these reduction waves were ascribed to the reduction of the anthraquinone and dppz units. However, it was difficult to identify which wave corresponds to the reduction of the anthraquinone unit.

Discussion

Synthetic Strategy. The parent complex, $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$, was successfully synthesized from 7-amino-dppz and $[RuCl_2(bpy)_2]$ in high yield. The Ru(II) polyimine center has an excellent excited state functionality suitable for the photosensitizing unit, and 7-amino-dppz has a rigid and extended π conjugation system suitable for the relay unit in the photoinduced energy/electron-transfer system.

The complex was stable enough for a further modification of the ligand, and photoinduced energy transfer systems were easily prepared by coupling with various energy-accepting units having a carboxylic acid group through the amide bond. Alternatively, the reaction of 7-amino-dppz with acid chloride and a subsequent reaction with $[RuCl_2(bpy)_2]$ also gave the same Ru(II) complex. However, the former synthetic strategy is more advantageous for preparing a series of complexes having different energy-accepting units, since products are obtained by only a one-step reaction from the key building unit, $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$.

Photoinduced Energy Transfer within the Complexes. Unlike the complex $[Ru(bpy)_2(dppz)]^{2+}$, whose relative emission intensity was 0.82 compared to that of [Ru-

Table 2. Electrochemical Data of Ru(II) Complexes in Acetonitrile at 25 °C

Complexes	Redox potentials $E°_{298}$/V vs. SCE		
	Oxidations/Ru^{3+}/Ru^{2+}	Os^{3+}/Os^{2+}	Reductions
$[Ru(bpy)_2(dppz)]^{2+}$	1.26		−1.00, −1.47
	1.24[a)]		−1.02,[a)] −1.44,[a)] −1.67,[a)] −2.07[a)]
$[RuAT]^{2+}$	1.26		−1.04, −1.45
$[RuAC]^{2+}$	1.25		−0.93, −1.31
$[RuAPQ]^{2+}$	1.25		−0.90, [−1.10][b)]
$[RuAQ]^{2+}$	1.25		[−0.83],[b)] [−1.01][b)]
$[RuAA]^{2+}$	1.27		−1.04, −1.46
$[RuAB]^{2+}$	1.25		[−1.01],[b)] −1.28[c)]
$[RuABOs]^{4+}$	1.25	0.83	[−0.94],[b)] −1.34[c)]

a) See the Ref. 11. b) Peak potential of the reduction wave. c) Irreversible.

(bpy)$_3$]$^{2+}$,[11] [Ru(bpy)$_2$(dppz-NH$_2$)]$^{2+}$ showed no emission either from the Ru(II) polypyridyl or the ligand center, though 7-amino-dppz itself was fluorescent. Apparently, excited energy quenching took place within the 7-amino-dppz ligand, but reason for this quenching effect is not clear yet. However, when the amide derivative of dppz, 7-(4-t-butylbenzoylamino)-dppz (AT), was used instead of 7-amino-dppz, the emission intensity was restored and was comparable to that of [Ru(bpy)$_3$]$^{2+}$. [RuAC]$^{2+}$ also showed reasonably strong emission, but [RuAQ]$^{2+}$, [RuAA]$^{2+}$, and [RuAPQ]$^{2+}$ showed very weak or almost no emission, suffering effective quenching of the emission from the Ru(II) polypyridyl center. Anthraquinone has been frequently used as an electron/energy acceptor and, therefore, the observed emission quenching may be due to electron/energy transfer to the anthraquinone unit. This is further supported by comparing the emission properties of [RuAT]$^{2+}$, [RuAC]$^{2+}$, and [RuAPQ]$^{2+}$. The structural difference of these complexes is only the substituent at the 4-position of the phenyl group of the acid component, and any effect on the electronic state of the dppz unit must be small. As shown in Table 2, the reduction potentials of the dppz moieties of these complexes were not much different from each other, and no direct correlation between the redox potentials and emission intensities was observed at all. Therefore, the observed emission quenching of [RuAPQ]$^{2+}$ is not ascribed to an alteration of the electronic state of the dppz unit, but to the energy or electron transfer to the anthraquinone unit in the acid moiety.

Anthraquinone is a well-known electron acceptor[12,13] (reduction potential −0.79—−0.83 V vs. SCE),[12] and could serve as a good excited electron trap. Therefore, the observed emission quenching of the excited Ru(II) center in [RuAQ]$^{2+}$ and [RuAPQ]$^{2+}$ can be explained as excited electron transfer to the anthraquinone unit. However, we could not confirm from the cyclic voltammogram that the reduction potential of the anthraquinone unit was higher than that of the dppz unit. The phosphorescence spectra of 2-substituted anthraquinones in ethanol at 77 K were generally a broad band having its maximum at around 500 nm, and has been reported to have a long tail down to 700 nm.[14] In the case of 2-(*N*-phenyl)carboxamidoanthraquinone, the lowest energy peak appeared at 588 nm.[14] Though the lowest energy peak of this anthraquinone derivative is still higher compared to the emission energy of the Ru(II) polypyridyl center, a sufficient spectral overlap may be expected. Therefore, we could not determine at this stage that the emission quenching of [RuAQ]$^{2+}$ and [RuAPQ]$^{2+}$ was due to an electron transfer or energy transfer to the anthraquinone unit.

In the case of anthracene, the electron affinity is not sufficiently high (−2.0 V vs. SCE),[15] but the triplet excited level is reported to be 682 nm.[16] Therefore, anthracene is capable of accepting the excited energy from the ^{3}MLCT state of the excited Ru(II) center. Thus, the observed emission quenching is most likely to be due to the triplet–triplet excited energy transfer to the anthracene unit.

This view is further supported by the emission properties of heterodinuclear [RuABOs]$^{4+}$. Though the emission from the Ru(II) polypyridyl center was relatively strong in mononuclear [RuAB]$^{2+}$, the complexation of Os(II) to [RuAB]$^{2+}$ caused quenching of the emission from the Ru(II) polypyridyl center along with a small increase of that from the Os(II) polypyridyl center. From the lifetimes of the emission from the Ru(II) polypyridyl center of [RuAB]$^{2+}$ (τ°) and [RuABOs]$^{4+}$ (τ), the rate of energy transfer (k_{en}) was estimated to be 1.0×10^8 s^{-1} ($k_{\mathrm{en}} = 1/\tau - 1/\tau^\circ$),[17] which is comparable to those reported for other photoinduced energy-transfer systems.[17]

To construct effective energy-transfer systems, it is necessary to tune the structural and electronic properties of the connector units between the donor and the acceptor units. For this purpose, a variety of bridging units have been designed and synthesized, most of which have rigid structures and/or extended π conjugation systems.[18] Though flexible and nonconjugation systems are also used as the connecting unit, they are generally less effective[19] compared to the rigid and π-conjugation systems. Amide bond has been proven to be effective as the connecting bond for energy- or electron-transfer systems.[17,20,21] Since an amide bond can be easily prepared, the use of an amide bond in the connection unit offers a convenient way to construct energy/electron-transfer systems if the structural and electronic properties are properly tuned.[18] In this study, we developed a novel building block having a photosensitizing unit (the Ru(II) polypyridyl center), a rigid connector unit (dppz), and a reactive amino group within the molecule. Thus, a variety of acceptor units could easily be attached directly to the rigid dppz unit through the amide bond; the resultant dppz-amide unit was shown to serve as an effective connector in the energy-transfer system. These results demonstrated that the [Ru(bpy)$_2$(dppz-NH$_2$)]$^{2+}$ complex is a useful building block for constructing efficient energy-transfer systems.

Experimental

Materials. [Ru(bpy)$_3$]Cl$_2$·6H$_2$O was supplied from Aldrich Chemical Co. and was recrystallized twice from methanol. [Ru(bpy)$_2$(dppz)]$^{2+}$ was synthesized according to a reported method.[6c] Other chemicals were obtained commercially and were used as received. The solvents used for spectral measurements were of fluorometric grade, supplied from Kanto Chemical Co. For column chromatography, active and neutral aluminum oxides with 70–230 mesh ASTM, or Sephadex LH-20 (Pharmacia) were used. In addition, for preparative thin-layer chromatography, silica or aluminum oxide (Merck) was used.

Measurements. The ^{1}H NMR spectra of samples in acetone-d_6 were recorded on a JEOL 500 FT NMR spectrometer. The absorption spectra were measured with a Shimadzu UV-2500 spectrophotometer at 25 °C, and the emission spectra with a Shimadzu RF-5300 spectrofluorometer at 25 °C. The emission intensities of the sample solutions (1.00×10^{-6} mol dm^{-3}, λ_{em} = 440 nm) were normalized by their absorbance at 440 nm, and were reported relative to that of 1.00×10^{-6} mol dm^{-3} [Ru(bpy)$_3$]Cl$_2$ in aqueous solution (Φ = 0.04).[22] In the case of the Ru(II)/Os(II) complex, the emission intensity from the Os(II) center was reported relative to that of 1.00×10^{-6} mol dm^{-3} [Os(bpy)$_2$(bdbpa)]$^{2+}$. The time-resolved emission decay was measured by exciting samples in acetonitrile with a nitrogen laser pulse (337 nm) through a coumarin chromophore (447 nm). The emission was then dispersed with a Hamamatsu Photonics C-2830 disperser and monitored on a Hamamatsu Photonics M-2548 streak camera. All samples were deoxygenated by the freeze-thaw cycle system before conducting a lifetime measurement.

Cyclic voltammetry was carried out at 25 °C in actonitrile containing 1.00×10^{-1} mol dm^{-3} tetrabutylammonium perchlorate as a supporting electrolyte using a Nikko Keisoku NPG FZ-2501-A potentiogalvanostat (sweep rate 50—200 mV s^{-1}). Each sample (5.00×10^{-4} mol dm^{-3}) was deoxygenated by N_2 bubbling before a measurement. The average of the anodic and corresponding cathodic peaks was reported as the redox potential (vs. SCE). Glassy carbon and platinum electrodes were used as working and counter electrodes, respectively, and a Ag/Ag$^+$ type RE-5 electrode (BAS Inc., 0.248 V vs. SCE) was used as a reference electrode. Ferrocene (0.41 V vs. SCE) was used for calibration, and the observed potentials were reported as those vs. SCE.

Ligands. 7-Amino-dppz and 7-(4-*t*-butylbenzoylamino)-dppz were prepared according to a previously reported procedure.[9]

2,2′-Bipyridine-4,4′-di(4-*t*-butylphenylamide) (bdbpa): 2,2′-Bipyridine-4,4′-dicarboxylic acid (0.1 g, 0.41mmol) was chlorinated by refluxing in thionyl chloride (8 ml) for 19 h under a N_2 atmosphere. After the reaction, thionyl chloride was removed and the product was reacted with 4-*t*-butylaniline (0.5 ml, 3.14 mmol) by refluxing in dry pyridine (5 ml) for 13 h at 85 °C under a N_2 atmosphere. After evaporating pyridine, a white precipitate appeared upon the addition of methanol. After that, it was filtered, washed by methanol, and dried in a vacuum oven at 80 °C: white powder (150 mg, yield: 72%). Mp 265—268 °C. ^{1}H NMR (DMSO-d_6, 500 MHz) δ = 1.36 (s; 18H, *t*-butyl), 7.47 (d, J = 8.9 Hz, 4H, *m*-phenyl), 7.79 (d, J = 8.6 Hz, 4H, *o*-phenyl), 8.04 (d, J = 4.9 Hz, 2H, 6,6′-bpy), 8.98 (s, 2H, 3,3′-bpy), 9.01 (d, J = 5.2 Hz, 2H, 5,5′-bpy), 10.73 (s, 2H, amide). Mass (FAB) *m/z* MH$^+$, 507.

Photosensitizing Unit [Ru(bpy)$_2$(dppz-NH$_2$)]$^{2+}$. To a 2-methoxyethanol (40 ml) solution of 7-amino-dppz (200 mg, 0.67 mmol), [RuCl$_2$(bpy)$_2$] (326 mg, 0.67 mmol) was added and reacted by refluxing for 13 h under a N_2 atmosphere. After solvent evaporation, small amounts of acetone and water were added to the residue, followed by the addition of an aqueous NH_4PF_6 solution. The precipitate was collected and washed by water. After drying, the precipitate was separated and purified by a Sephadex LH-20 column (diameter 2 cm, length 16 cm) with acetonitrile as an eluent. The obtained complex was dried in a vacuum oven at 80 °C: dark-brown, fine needles (620 mg as a PF_6 salt, yield: 92%); ^{1}H-^{1}H COSY (acetone-d_6, 500 MHz) δ = 6.34 (s, 1H, NH$_2$), 7.33 (s, 1H, 6), 7.41—7.44 (2H, bpy), 7.63—7.66 (2H, bpy), 7.72 (d, J = 9.2 Hz, 1H, 8 or 9), 7.97—8.02 (2H, 3, 12), 8.08—8.10 (2H, bpy), 8.14—8.19 (5H, 8 or 9, bpy), 8.25—8.29 (2H, bpy), 8.40—8.48 (2H, 2, 13), 8.83—8.88 (4H, bpy), 9.56—9.62 (2H, 4, 11). Mass (FAB) *m/z* [M−PF$_6$], 856, [M−(PF$_6$)$_2$], 711. Anal. Calcd for $C_{39}H_{29}N_9F_{12}OP_2Ru$ including 1 mol water: C, 44.80; H, 2.87; N, 12.37%. Found: C, 45.05; H, 2.89; N, 12.64%.

[RuAT]$^{2+}$. To a dimethylacetamide (DMA) (5 ml) solution of [Ru(bpy)$_2$(dppz-NH$_2$)]$^{2+}$ (30 mg, 0.03 mmol), 4-*t*-butylbenzoyl chloride (0.1 ml, 0.5 mmol) was added and reacted by refluxing for 25 h under a N_2 atmosphere. After the solvent was evaporated to dryness, a crude compound was converted to a PF_6 salt as follows. The precipitate was collected and washed by water. The obtained complex was purified by an alumina column (diameter 2 cm, length 15 cm) with acetonitrile including NH_4PF_6 (8 mg ml^{-1}) as an eluent. After evaporating to dryness, reprecipitation by the addition of water, filtration, and successive washing with water and diethyl ether gave a purified complex, which was dried in a vacuum oven at 80 °C: brown powder (22 mg as a PF_6 salt, yield: 63%); ^{1}H NMR (acetone-d_6, 500 MHz) δ = 1.39 (s, 9H), 7.42—7.46 (2H), 7.64—7.68 (5H), 8.05—8.21 (9H), 8.29 (t, J = 8.0 Hz, 2H), 8.43—8.48 (2H), 8.54 (d, J = 5.4 Hz, 1H), 8.56 (d, J = 5.2 Hz, 1H), 8.86—8.90 (4H), 9.27 (s, 1H), 9.71 (d, J = 8.2 Hz, 1H), 9.78 (d, J = 7.9 Hz, 1H), 10.24 (s, 1H). Anal. Calcd for $C_{49}H_{45}N_9F_{12}O_4P_2Ru$ including 3 mol water: C, 48.44; H, 3.73; N, 10.38%. Found: C, 48.41; H, 3.49; N, 10.44%.

Alternatively, this complex was also prepared by the following reaction. 7-(4-*t*-Butylbenzoylamino)-dppz (63 mg, 0.14 mmol) and [RuCl$_2$(bpy)$_2$] (63 mg, 0.13 mmol) were reacted in deareated aqueous ethanol (ethanol : H_2O = 1 : 1, 30 ml) by refluxing for 3 h under a N_2 atmosphere. The solvent was then evaporated to dryness, and a crude compound was converted to a PF_6 salt. The precipitate was collected and washed with water, and was purified by a Sephadex LH-20 column with acetonitrile as an eluent to give the complex (147 mg as a PF_6 salt, yield: 97%).

[RuAC]$^{2+}$. To a DMA (10 ml) solution of [Ru(bpy)$_2$(dppz-NH$_2$)]$^{2+}$ (80 mg, 0.08 mmol), 4-cyanobenzoyl chloride (72 mg, 0.44 mmol) was added and reacted by refluxing for 29 h under N_2 atmosphere. After solvent evaporation, small amounts of acetone and water were added to the residue, followed by the addition of an aqueous NH_4PF_6 solution. The precipitate was collected and washed by water. The obtained complex was purified by alumina preparative TLC with acetonitrile including NH_4PF_6 (4 mg ml^{-1}) as an eluent. After evaporating to dryness, precipitation by the addition of small amounts of acetone and water, filtration, and washing with water and diethyl ether gave a purified complex, which was dried in a vacuum oven at 80 °C: orange powder (48 mg as a PF_6 salt, yield: 54%). ^{1}H NMR (acetone-d_6, 500 MHz) δ = 7.42—7.45 (2H), 7.65—7.68 (2H), 8.03—8.21 (10H), 8.27—8.31 (4H), 8.42—8.50 (2H), 8.54 (dd, J = 5.2 Hz, J' = 1.2 Hz, 1H), 8.56 (dd, J = 5.5 Hz, J' = 1.2 Hz, 1H), 8.85—8.90 (4H), 9.27 (s, 1H), 9.72 (d, J = 8.3 Hz, 1H), 9.79 (d, J = 8.1 Hz, 1H), 10.54 (s, 1H). Mass (FAB) *m/z*, [M−PF$_6$], 985, [M−(PF$_6$)$_2$], 840. Anal. Calcd for $C_{46}H_{34}N_{10}F_{12}O_3P_2Ru$ including 2 mol water: C, 47.39; H, 2.94; N, 12.01%. Found: C, 47.53; H, 2.78; N, 11.58%.

[RuAPQ]$^{2+}$ 4-(2-Amideanthraquinone)benzoic Acid: 2-Carboxylic anthraquinone (1 g, 3.96 mmol) was reacted in thionyl chloride (9 ml) at 90 °C for 13 h under N_2 atmosphere. Resultantly, the acid chloride was obtained by evaporating thionyl chloride and drying, and was immediately used in a reaction with 4-aminobenzoic acid (0.55 g, 4.01 mmol) in dry benzene (40 ml) at 95 °C for 3 h under a N_2 atmosphere. A white precipitate was formed on reaction, which was collected by filtration and washed by benzene and water. It was purified by hot filtration and recrystallization from ethyl acetate, and dried in a vacuum oven at 80 °C: white powder (1.1 g, yield: 73%). mp 337—338 °C. ^{1}H NMR (DMSO-d_6, 500 MHz,) δ = 8.01—8.05 (6H), 8.31—8.35 (2H), 8.41—8.43 (1H), 8.51—8.53 (1H), 8.83 (s, 1H), 11.04 (s, 1H). Mass: HR-MS; Found: *m/z* 371.0806. Calcd for $C_{22}H_{13}NO_5$: M, 371.0794.

4-(2-Amideanthraquinone)benzoic acid (32 mg, 0.086 mmol) was chlorinated by thionyl chloride (15 ml) at 95 °C for 20 h under a N_2 atmosphere. To a DMA (10 ml) solution of [Ru(bpy)$_2$(dppz-NH$_2$)]$^{2+}$ (80 mg, 0.08 mmol), the thus-obtained acid chloride was immediately added and reacted by refluxing for 62 h under a N_2 atmosphere. [RuAPQ]$^{2+}$ was obtained by the same method as that for [RuAC]$^{2+}$: orange powder (35 mg as a PF_6 salt, yield: 32%). ^{1}H NMR (acetone-d_6, 500 MHz) δ = 7.44—7.48 (2H), 7.66—7.69 (2H), 7.92—7.96 (2H), 8.03—8.36 (18H), 8.42—8.45 (2H), 8.46—8.58 (2H), 8.74—8.78 (1H), 8.87—8.91 (4H), 9.22 (s, 1H), 9.63 (d, *J* = 8.0 Hz, 1H), 9.76 (d, *J* = 8.0 Hz, 1H), 10.24 (s, 1H), 10.34 (s, 1H). Anal. Calcd for $C_{60}H_{44}N_{10}F_{12}O_7P_2Ru$ including 3 mol water: C, 51.18; H, 3.15; N, 9.95%. Found: C, 51.60; H, 3.40; N, 9.25%.

[RuAQ]$^{2+}$. 2-Carboxylic anthraquinone (25 mg, 0.1 mmol) was chlorinated by refluxing in thionyl chloride (3 ml) for 15 h under a N_2 atmosphere. After the reaction, thionyl chloride was removed and the product was reacted with $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ (60 mg, 0.06 mmol) by refluxing in DMA (7 ml) for 91 h under N_2 atmosphere. The same procedure as that for $[RuAC]^{2+}$ gave a product: orange powder (55 mg as a PF_6 salt, yield: 75%). ^{1}H NMR (acetone-*d*$_6$, 500 MHz) δ = 7.47—7.52 (2H), 7.67—7.69 (2H), 7.78—8.00 (4H), 8.06—8.09 (1H), 8.16—8.41 (12H), 8.50—8.58 (3H), 8.75 (s, 1H), 8.87—8.92 (4H), 9.10 (s, 1H), 9.48 (d, *J* = 8.0 Hz, 1H), 9.66 (d, *J* = 8.0 Hz, 1H), 10.70 (s, 1H). Anal. Calcd for $C_{53}H_{37}N_9F_{12}O_5P_2Ru$ including 2 mol water: C, 50.09; H, 2.93; N, 9.92%. Found: C, 49.93; H, 2.93; N, 9.62%.

[RuAA]$^{2+}$. 9-Carboxylic anthracene (16 mg, 0.07 mmol) was chlorinated by refluxing in thionyl chloride (5 ml) for 7 h under a N_2 atmosphere. After the reaction, thionyl chloride was removed and the residual acid chloride was reacted with $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ (42 mg, 0.04 mmol) by refluxing in DMA (10 ml) for 50 h under N_2 atmosphere: orange powder (8 mg as a PF_6 salt, yield: 17%). ^{1}H NMR (acetone-*d*$_6$, 500 MHz) δ = 7.41—7.44 (3H), 7.65—7.68 (3H), 8.06—8.21 (13H), 8.27—8.30 (2H), 8.41—8.43 (1H), 8.52—8.56 (3H), 8.85—8.90 (6H), 9.12 (s, 1H), 9.71 (dd, *J* = 8.2 Hz, *J'* = 1.5 Hz, 1H), 9.78 (dd, *J* = 8.2 Hz, *J'* = 1.5 Hz, 1H), 10.02 (s, 1H). Anal. Calcd for $C_{53}H_{35}N_9F_{12}OP_2Ru$ including 1 mol water: C, 52.05; H, 2.89; N, 10.31%. Found: C, 51.96; H, 2.95; N, 10.10%.

[RuAB]$^{2+}$. 2,2′-Bipyridine-4,4′-dicarboxylic acid (52 mg, 0.21 mmol) was chlorinated by refluxing in thionyl chloride (6 ml) for 13 h under a N_2 atmosphere. After the reaction, thionyl chloride was removed and the product was reacted with $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ (30 mg, 0.03 mmol) by refluxing in DMA (5 ml) for 14 h under a N_2 atmosphere. The obtained product was separated and purified by alumina preparative TLC using an eluent of acetonitrile containing NH_4PF_6 (4 mg ml^{-1}): orange powder (10 mg as a PF_6 salt, yield: 26%). ^{1}H NMR (acetone-*d*$_6$, 500 MHz) δ = 3.05 (s, 3H), 3.12 (s, 3H), 7.42—7.46 (2H), 7.52 (s, 1H), 7.66—7.68 (2H), 8.08—8.22 (9H), 8.28—8.31 (2H), 8.46—8.58 (5H), 8.85—8.91 (5H), 8.94 (d, *J* = 4.9 Hz, 1H), 9.04 (s, 1H), 9.34 (s, 1H), 9.74 (dd, *J* = 8.2 Hz, *J'* = 1.2 Hz, 1H), 9.82 (dd, *J* = 8.3 Hz, *J'* = 1.2 Hz, 1H), 10.78 (s, 1H). Mass (FAB) *m*/*z* [M−PF$_6$], 1109, [M−PF$_6$−HPF$_6$], 963. Anal. Calcd for $C_{52}H_{42}N_{12}F_{12}O_4P_2Ru$ including 2 mol water: C, 48.43; H, 3.28; N, 13.03%. Found: C, 48.25; H, 3.06; N, 12.45%.

[RuABOs]$^{4+}$. To a 2-methoxyethanol solution (5 ml) of $[RuAB]^{2+}$ (11.5 mg, 0.009 mmol), $Os(bpy)_2Cl_2$ (7.5 mg, 0.013 mmol) was added and reacted by refluxing for 14 h under a N_2 atmosphere. After evaporating the solvent, the product was separated and purified by silica preparative TLC using an eluent of acetonitrile containing NH_4PF_6 (4 mg ml^{-1}): dark-greenish powder (8 mg as a PF_6 salt, yield: 44%). ^{1}H NMR (acetone-*d*$_6$, 500 MHz) δ = 3.05 (s, 3H), 3.08 (s, 3H), 7.41—7.44 (2H), 7.50—7.57 (5H), 7.65—7.68 (2H), 7.95—8.20 (18H), 8.27—8.31 (3H), 8.38 (dd, *J* = 9.4 Hz, *J'* = 2.4 Hz, 1H), 8.52—8.57 (3H), 8.83—8.89 (8H), 8.94 (s, 1H), 9.21 (s, 1H), 9.44 (s, 1H), 9.74 (dd, *J* = 8.2 Hz, *J'* = 1.2 Hz, 1H), 9.81 (dd, *J* = 8.3 Hz, *J'* = 1.2 Hz, 1H), 10.55 (s, 1H). Mass (MALDI-TOF) *m*/*z* [M−PF$_6$], 1903, [M−PF$_6$−HPF$_6$], 1757, [M−PF$_6$−(HPF$_6$)$_2$], 1611, [M−PF$_6$−(HPF$_6$)$_3$], 1465. Anal. Calcd for $C_{72}H_{56}N_{16}F_{24}O_3P_4RuOs$ including 2 mol water: C, 41.53; H, 2.79; N, 10.76%. Found: C, 42.12; H, 2.83; N, 10.14%.

[Os(bpy)$_2$(bdbpa)]$^{2+}$. To a 2-methoxyethanol (10 ml) solution of 2,2′-bipyridine-4,4′-di(4-*t*-butylphenylamide) (30 mg, 0.059 mmol), $[OsCl_2(bpy)_2]$ (35 mg, 0.061 mmol) was added and reacted by refluxing for 24 h under a N_2 atmosphere. After evaporating the solvent, it was separated and purified by alumina column chromatography using an eluent of acetone : H_2O = 49 : 1: dark greenish powder (63 mg as a PF_6 salt, yield: 82%). ^{1}H NMR (acetone-*d*$_6$, 500 MHz) δ = 1.31 (s, 18H), 7.39 (d, *J* = 8.2 Hz, 4H), 7.52—7.58 (4H), 7.85 (d, *J* = 5.2 Hz, 2H), 7.95 (d, *J* = 7.7 Hz, 4H), 8.01 (d, *J* = 5.5 Hz, 2H), 8.07—8.11 (8H), 8.16 (d, *J* = 5.5 Hz, 2H), 8.85—8.88 (4H), 10.19 (1H), 10.52 (1H). Mass (FAB) *m*/*z* [M−PF$_6$], 1155, [M−PF$_6$−HPF$_6$], 1009. Anal. Calcd for $C_{52}H_{50}N_8F_{12}O_2P_2Os$ including 1 mol water: C, 47.39; H, 3.94; N, 8.50%. Found: C, 47.64; H, 3.83; N, 8.18%.

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