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Photophysical and Redox Properties of Dinuclear Ru(II) Complexes Prepared from the Photosensitizing Unit $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ (dppz-NH_2: 7-amino-dipyrido[3,2-*a*:2',3'-*c*] phenazine)

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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] In particular, it has been reported previously in our group[5] that 7-amino-dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz-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 electron/energy-transfer systems. Herein, we synthesized the dinuclear Ru(II) complexes $[Ru_2AP]^{4+}$ and $[Ru_2AE]^{4+}$ as the moderate yield by one-pot amide formation with $Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ and terephthaloyl chloride or fumaryl chloride, respectively, for the construction of the long-ranged photoinduced electron/energy-transfer systems, as shown in Figure 1. Thus, we studied the photophysical and electrochemical properties of $[Ru_2AP]^{4+}$ and $[Ru_2AE]^{4+}$, respectively. The parent complex, $[Ru(bpy)_2$-$(dppz\text{-}NH_2)]^{2+}$ used as a photosensitizing unit, was easily prepared in high yield (86%) from $Ru(bpy)_2Cl_2$ and 7-amino-dppz by one-step reaction as reported previously.[5]

Dinuclear complexes could be purified through the best selection of an alumina column or alumina preparative TLC with ammonium hexafluorophosphate/acetonitrile solution as an eluent. The dinuclear complexes obtained as PF_6 salts were orange to brown powders and attempts to crystallize from various solvents were unsuccessful. All the complexes were characterized by ^{1}H-NMR and elemental analyses. Since the structures of the complexes were similar to each other, their structures were successfully interpreted from ^{1}H-NMR spectra.

As the synthetic strategy, within the complex, the Ru(II) polyimine center had the excellent excited state functionality suitable for the photosensitizing unit. While, 7-amino-dppz had a rigid and extended π conjugation system suitable for the relay unit in the photoinduced energy/electron transfer system.

Absorption spectra of the complexes (1.00×10^{-5} mol dm^{-3})

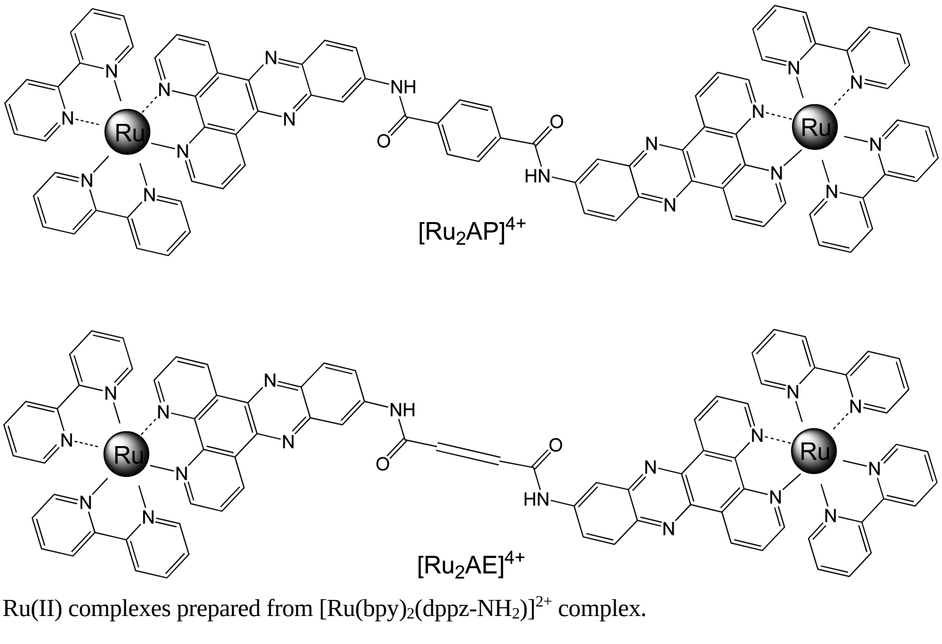

Figure 1. Dinuclear Ru(II) complexes prepared from $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ complex.

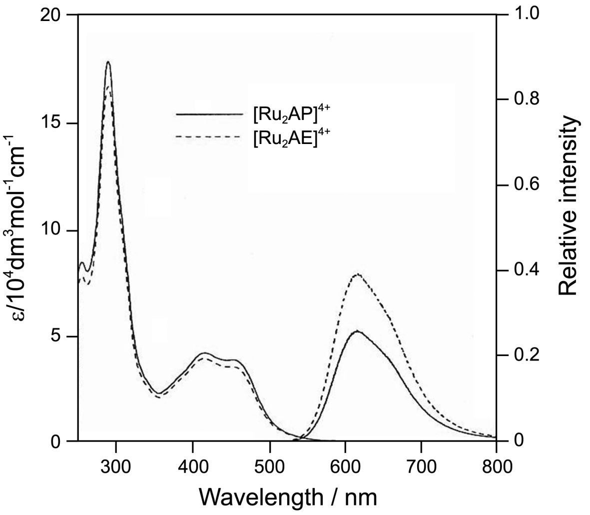

Figure 2. Absorption and emission spectra of dinuclear Ru(II) complexes in acetonitrile at 25 °C.

were measured in acetonitrile at 25 °C together with their emission spectra, as shown in Figure 2. A broad band between 350 nm and 500 nm was composed of both the ligand-centered π-π*/n-π* absorption band of the 7-amino-dppz ligand[6] and the spin-allowed metal-to-ligand charge transfer (MLCT) band from the Ru(II) center to the diimine ligands.[7] The ligand-centered π-π* transition was also observed at about 300 nm.[6] Absorption spectral data of these complexes are summarized in Table 1. The spin-allowed MLCT bands of these complexes are similar to each other. Emission spectra of the complxes (1.00×10^{-6} mol dm^{-3}) by excitation at 440 nm were measured in acetonitrile at 25 °C as shown in Figure 2, and the data are summarized in Table 1. Emission intensities of the Ru(II) complxes were normalized by the absorbance at 440 nm, and were reported as relative to that of $[Ru(bpy)_3]^{2+}$. The emission band of the Ru(II) complexes appeared at around 610 nm, and their emission intensities were very high relative to that of parent complex $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ as shown in Table 1. Since fluorescence of 7-amino-dppz appeared at 534 nm,[6] the observed emission of Ru(II) complex seems being derived mostly from the Ru(II) polyimine center, not from 7-amino-dppz.

Table 1. Absorption and emission data of Ru(II) complexes in acetonitrile at 25 °C

Complexes	Absorption λ_{max}/nm (ε/10^4 dm^3 mol^{-1} cm^{-1})				Emission λ_{max}/nm (intensity)[a]
$[Ru(bpy)_2$	468	318	288	257	610
$(dppz\text{-}NH_2)]^{2+}$ [b]	(2.50)	(4.46)	(7.26)	(4.57)	(0.03)
$[Ru_2AP]^{4+}$	451^{sh}	415	289	256	616
	(3.89)	(4.22)	(17.91)	(8.52)	(0.26)
$[Ru_2AE]^{4+}$	450^{sh}	412	289	256	616
	(3.56)	(3.94)	(16.72)	(7.86)	(0.40)

[a] Intensities are relative to data of 1.00×10^{-6} mol dm^{-3} $[Ru(bpy)^3]^{2+}$ in aqueous solution at λ_{ex} = 440 nm. [b] See the Ref. 5.

Table 2. Electrochemical data of Ru(II) complexes in acetonitrile at 25 °C

Complexes	Redox potentials E^o_{298}/V *vs* SCE		
	Oxidations/Ru^{3+}/Ru^{2+}	Reductions	
$[Ru(bpy)\,(dppz\text{-}NH_2)]^{2+}$	1.26	−1.02,	−1.48
$[Ru_2AP]^{4+}$	1.27	−1.06,	−1.45[a]
$[Ru_2AE]^{4+}$	1.27	−1.01[b]	−1.48[a]

[a] Irreversible. [b] Peak potential of the reduction wave.

The emission decay curve of Ru(II) complexes was measured at 610 nm, and showed single exponential component. The life-time (t) of parent complex $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ showed shorter one as 95 ns, while the life-time of dinuclear Ru(II) complexes $[Ru_2AP]^{4+}$ and $[Ru_2AE]^{4+}$ showed longer ones as 172 ns and 185 ns, respectively.

Cyclic voltammetry of the complxes (5.00×10^{-4} mol dm^{-3}) in acetonitrile was carried out in the range between +1.47 V to −2.28 V *vs* SCE at 25 °C, and their results were summarized in Table 2. In the positive region, all the complexes had reversible one-electron redox peaks due to a Ru^{2+}/Ru^{3+} couple at +1.25 ~ +1.27 V *vs* SCE,[1d] and no other redox peaks were observed up to +1.47 V *vs* SCE. The two metal centers of dinuclear complex underwent simultaneously the redox process since the peak intensities were approximately twice higher than their mononuclear analogs. Therefore, no direct metal-metal interaction was observed electrochemically in the dinuclear complex. In the negative region, the parent complex $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ showed reversible first reduction couples at −1.00 V *vs* SCE and has been ascribed to the reduction of the phenazine unit.[8] Similar reversible first reduction couples was observed for $[Ru_2AP]^{4+}$, while irreversible wave was observed with only the reduction wave for $[Ru_2AE]^{4+}$.

In conclusion, since amide bond can be easily prepared for dinuclear complex, use of the amide bond in the connection unit offers convenient way for construction of long-ranged energy/electron transfer systems if the structural and electronic properties are properly tuned. Thus, the above results demonstrated that $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ complex is the useful building block for construction of efficient energy/electron transfer systems.

Experimental Section

Materials. $Ru(bpy)_3Cl_26H_2O$ was supplied from Aldrich Chemical Co. and was recrystallized twice from methanol. $[Ru(bpy)_2(dppz)]^{2+}$ was synthesized according to the reported method.[5] Other chemicals were obtained commercially and were used as received. Solvents used for the spectral measurements were the 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 the preparative thin layer chromatography, the silica or aluminum oxide (Merck) was used.

Measurements. Absorption spectra were measured with a Shimadzu UV-2500 spectrophotometer at 25 °C, and emission spectra with a Shimadzu RF-5300 spectro-fluorometer at 25 °C.

Emission intensities of the sample solutions (1.00×10^{-6} mol dm^{-3}, $\lambda_{em} = 440$ nm) were normalized by their absorbance at 440 nm, and were reported relative to that of 1.00×10^{-6} mol dm^{-3} $Ru(bpy)_3Cl_2$ in aqueous solution ($\phi = 0.04$). The time-resolved emission decay was measured by exciting the samples in acetonitrile with a nitrogen laser pulse (337 nm) filtering off as a coumarin chromophore (447 nm). The emission was then dispersed with a Hamamatsu Photonics C-28 disperser and monitored on a Hamamatsu Photonics M-25 streak camera. All samples were deoxygenated by the freeze-thaw cycle system before a life-time measurement. Cyclic voltammetry was carried out at 25 °C in acetonitrile 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 mVs^{-1}). Each sample (5.00×10^{-4} mol dm^{-3}) was deoxygenated by N_2 bubbling before measurement. Average of 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) as a reference electrode. Ferrocene (0.41 V *vs* SCE) was used for calibration, and observed potentials were reported as those vs SCE.

Syntheses. Photosensitizing unit, $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ was prepared as reported previously.[5]

$[Ru_2AP]^{4+}$. To a DMA (6 mL) and dehydrated pyridine (3 mL) solution of $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ (60 mg, 0.06 mmol), terephthaloyl chloride (5 mg, 0.02 mmol) was added and reacted by refluxing for 25 h under N_2 atmosphere: orange powder (38 mg, yield 75%), ^{1}H-NMR (acetone-*d*$_6$, 500 MHz) δ 7.43 (t, *J* = 6.5 Hz, 4H), 7.66 (t, *J* = 6.5 Hz, 4H), 8.03-8.20 (22H), 8.26-8.29 (4H), 8.33-8.35 (2H), 8.51 (d, *J* = 5.2 Hz, 2H), 8.53 (d, *J* = 5.2 Hz, 2H), 8.84-8.89 (8H), 9.00 (s, 2H), 9.62-9.66 (4H), 9.98 (s, 2H); Anal. Calcd for $C_{84}H_{68}N_{18}F_{24}O_8P_4Ru_2$ including 6 mol water: C, 45.05; H, 3.06; N, 11.26%. Found: C, 44.67; H, 2.95; N, 11.46%.

$[Ru_2AE]^{4+}$. To a DMA (5 mL) and dehydrated pyridine (2 mL) solution of $[Ru(bpy)_2(dppz\text{-}NH_2)]^{2+}$ (65 mg, 0.07 mmol), fumaryl chloride (diluted 0.1 mL, 0.03 mmol) was added and reacted by refluxing for 25 h under N_2 atmosphere: orange powder (42 mg, yield: 67 %); ^{1}H-NMR (acetone-d$_6$, 500 MHz) δ 7.42-7.45 (4H), 7.64-7.67 (4H), 8.02-8.20 (20H), 8.26-8.29 (4H), 8.32-8.34 (2H), 8.49-8.53 (4H), 8.84-8.89 (8H), 8.98 (s, 2H), 9.61-9.64 (4H), 9.98 (s, 2H); Anal. Calcd for $C_{80}H_{60}N_{18}F_{24}O_5P_4Ru_2$ including 3 mol water: C, 45.00; H, 2.83; N, 11.81%. Found: C, 45.17; H, 3.03; N, 11.66%.

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