Synthesis and Light-Harvesting Functions of Ring-Shaped Re(I) Trinuclear Complexes Connected with an Emissive Ru(II) Complex

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ABSTRACT: Ring-shaped Re(I) multinuclear complexes (Re(I) rings) in which Re(I)-diimine-biscarbonyl complexes are connected to each other through bisphosphine bridging ligands exhibit very suitable photophysical and electrochemical properties as redox photosensitizers. We developed two approaches for synthesizing Re(I) rings connected with a Ru(II) complex: cyclization of a linear Re(I) trinuclear complex connected with a Ru(II) complex and Mizoroki−Heck coupling of a ring-shaped Re(I) trinuclear complex and a Ru(II) complex. Photophysical measurements of these heteromultinuclear complexes and comparisons with their model complexes indicated that they exhibit efficient light-harvesting abilities, where energy transfer from the excited ring-shaped Re(I) trinuclear complex unit to the Ru(II) complex unit proceeds efficiently.

KEYWORDS: multinuclear complexes, luminescence, energy transfer, light-harvesting system, coupling reaction

INTRODUCTION

The systematic integration of emissive polypyridyl d-metal complexes potentially affords useful photophysical properties and/or photochemical behaviors that cannot be achieved using the corresponding mononuclear complexes, such as control of the direction and speed of excitation energy and/or electron transfer, photochemical multielectron accumulation, and good performance as redox photosensitizers or photocatalysts. As typical examples, wheel-type assemblies and dendrimers constructed with Ru(II) trisdimeine complexes; multiporphyrin arrays with Re(I) or Ru(II) ions; and ring-shaped multinuclear Re(I) complexes have been reported. Among them, ring-shaped Re(I) multinuclear complexes (Re(I) rings) in which Re(I)-diimine-biscarbonyl complexes are connected to each other through bisphosphine bridging ligands exhibit unique photophysical and electrochemical properties, e.g., strong luminescence from the triplet metal-to-ligand charge transfer (MLCT) excited state (emission quantum yield as high as 66%) and much longer lifetime (as high as 7.77 μs) and stronger oxidation power of the MLCT excited state compared with those of the corresponding mononuclear and linear-shaped multinuclear Re(I) complexes, and stability of both the excited state and the reduced state. Because of their excellent redox photosensitizer ability, the Re(I) rings have been used in the photocatalytic reduction of CO₂. For example, a photocatalytic system comprising a trinuclear Re(I) ring as a redox photosensitizer and a Re(I) mononuclear complex as a catalyst exhibits the highest quantum yield of CO₂ reduction in the reported photocatalytic systems (ΦCO₂ = 82%). In addition, tetranuclear Re(I) rings can photochemically accumulate as many as four electrons per molecule and their reduced state is stable. These useful photofunctions are reinforced by interligand π-π interaction between the diimine ligands and phenyl groups in the phosphine ligands. Such interaction is substantially enhanced when the multinuclear complexes are cyclized because of the rigidity of the molecular structure and the limited rotation along the P-Re-P bonds.

The synergistic connection of different photofunctional complexes to form heteromultinuclear complexes is a useful approach to creating new photofunctions that cannot be achieved using a simple mixture of the corresponding model complexes. The Re(I) rings should be fascinating candidates for such heteromultinuclear complexes because of their aforementioned unique photophysical and photochemical properties. Therefore, synthetic methods to introduce into the Re(I) rings another metal complex that does not affect the Re(I) rings’ steric structures should be developed to create a new class of photofunctional molecules.

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Figure 1. Structures and abbreviations of [Ring-Ru]5+’s and the model complexes. All are PF6− salts.

Scheme 1. Synthesis of [Ring-Ru1]5+ via Decarbonylation with Me3NO and Subsequent Cyclization with Bidentate Phosphine Ligands

1. AgOTf, CH2Cl2, reflux
2. P-P, CH2Cl2, reflux

Process A

Process B

Process C

L = solvent, Me3N
We herein report two methods for synthesizing such Re(I) rings connected with a Ru(II) trisdiimine complex, which is another type of useful photofunctional metal complex ([Ring-Ru]5+): (1) cyclization of linear-shaped Re(I) trinuclear complexes already connected to the Ru complex and (2) the Mizoroki–Heck reaction between a ring-shaped Re(I) trinuclear complex and a Ru(II) complex. The synthesized [Ring-Ru]5+’s exhibit excellent light-harvesting functions: light energy absorbed by the Re(I)-ring unit is efficiently transferred to the Ru unit. Figure 1 illustrates the structures of the synthesized [Ring-Ru]5+(n = 1, 2, 3) and the corresponding model complexes.

RESULTS AND DISCUSSION

Synthesis

(1) Cyclization of Linear Re(I) Trinuclear Complexes Connected with a Ru Complex. To substitute both terminal CO ligands in the linear-shaped Re(I) trimer complexes, which is one of the critical processes for synthesizing the target complexes, we recently developed a selective method for removing the carbonyl ligand only in the trans-position to the phosphine ligand in fac-[Re(N=N)(CO)3(PR3)]+ (N=N = dimine ligand) using Me3NO as a decarbonylation reagent.20,23 Notably, the photochemical ligand substitution reaction, which is well-known as the other method to remove CO ligands, cannot be used in the case of linear Re(I) multinuclear complexes with a Ru(II) unit because efficient energy transfer proceeds from the excited Re units to the Ru unit.30 As a typical example, the synthetic scheme for [Ring-Ru1]5+ is illustrated in Scheme 1. A linear Re trimer in which one of the edge Re moieties is connected with a Ru(II) complex ([L3(4dmb)(trans-CO)2-Ru(4dmb,bpy2)]5+, 4dmb = 4,4′-dimethyl-2,2′-bipyridine, bpy = 2,2′-bipyridine) was synthesized via the reaction between the Re dimer with a labile isolated [Ring-Ru1]5+. The synthesized [Ring-Ru1]5+ was isolated in 44% isolated yield. Its 1H NMR spectrum is shown in Figure 2. Similar procedures were applied to synthesize [Ring-Ru2]PF6 using [L3(5dmb)5+], (trans-CO)2-Ru(5dmb)PF6 (Scheme S1). The yield was estimated to be 64% on the basis of the amount of [R3et(5dmb,Brbpy)]5+ consumed, as determined by SEC analysis of the reaction solution. Purification using RSEC resulted in an isolated yield of 40%. Notably, the excess amount of [Ru(4dmb)2(allyl-4dmb)]2+ was necessary to

Figure 2. Aromatic region of the 1H NMR spectrum of [Ring-Ru1]5+ in CD3CN. The same numbering of the diimine moieties for the Ru complex is applied for the Re-ring.
supress a competitive reaction, i.e., homocoupling of [R3et(5dmb2,Brbpy)]3+. These synthesized ring–Ru complexes [Ring-Ru](n = 1, 2, 3) are the first examples of ring-shaped Re(I) multinuclear complexes modified with another metal complex. They were fully characterized by NMR, infrared (IR), and high-resolution mass spectroscopies. The corresponding trinuclear Re(I) rings without the Ru unit and the mononuclear Ru(II) trisdiimine complexes shown in Figure 1 were also synthesized as model compounds for clarifying photophysical processes of the ring–Ru complexes, as described in the next section.

Photophysical Properties

Figure 3 shows UV−Vis absorption spectra recorded in MeCN. The absorption spectra of all of the [Ring-Ru](n = 1, 2, 3) complexes were similar to a 1:1 summation spectrum of the singlet metal-to-ligand charge transfer (1MLCT) absorption bands of the Re(I) ring and Ru(II) model complexes (i.e., [Ring1]3+ + [Ru1]2+, [Ring2]3+ + [Ru2]2+, and [Ring3]3+ + [Ru3]2+, respectively). These results indicate that no strong electronic interaction occurred between the Re ring and Ru units. Notably, in the spectra of all of the [Ring-Ru](n = 1, 2, 3), the 1MLCT absorption band of the Ru(II) unit was observed at longer wavelengths compared with that of the Re(I)-ring unit.

All of the [Ring-Ru](n = 1, 2, 3) complexes are emissive in MeCN at ambient temperature. The photophysical properties of [Ring-Ru](n = 1, 2, 3) and the corresponding model complexes are summarized in Table 1. Figure 4a shows the emission spectra of [Ring-Ru]3+ as a typical example; these spectra were recorded using two different excitation wavelengths. The shape of the emission band varied according to the excitation wavelength: a shoulder was observed at λem ≈ 550 nm when [Ring-Ru]3+ was excited at λex = 380 nm, whereas the shoulder decreased in intensity when the complex was excited at λex = 469 nm. Mainly the Re ring unit and partially the Ru unit absorb the light at λex = 380 nm, whereas the light at λex = 469 nm is mainly absorbed by the Ru unit (Figure 3a). The maximum emission wavelength (λem,max) was 622 and 624 nm when the complex was excited at λex = 380 and 469 nm, respectively. Therefore, even though the excitation light should be absorbed mainly by the Re ring unit of [Ring-Ru]3+, the maximum emission wavelength was similar to that of [Ru1]2+ (λem,max = 630 nm) but not to that of [Ring1]3+ (λem,max = 581 nm) (Figure 4a). The emission spectrum of [Ring-Ru]3+ recorded with λex = 380 nm was well-simulated with the emission spectra of [Ru1]2+ and [Ring1]3+ (Figure 4b). The simulation also reveals that the main component of the emission from [Ring-Ru]3+ should be from the Ru unit but not from the Re ring unit and that the shoulder peak at λem ≈ 550 nm in the emission band of [Ring-Ru]3+ can be assigned to emission from the Re ring unit.

The emission quantum yield (Φem) was determined to be 11% (λex = 380 nm), which is slightly greater than that of [Ru1]2+ (Φem = 9%) but less than that of [Ring1]3+ (Φem = 15%). These results clearly indicate that energy transfer efficiently proceeded from the excited Re ring unit to the Ru
their excitation energy to the Ru unit, can be estimated by using eq 1:

$$\eta_{ET} = 100 - 100 \times \left( \frac{A_{\text{sim}(\text{Ring-Ru})}}{A_{\text{cm}(\text{Ring-Ru})}} \right) \div \left( \frac{\epsilon_{\text{Ring}}}{\epsilon_{\text{Ring}} + \epsilon_{\text{Ru}}} \right)$$

where $A_{\text{sim}(\text{Ring-Ru})}$ and $A_{\text{cm}(\text{Ring-Ru})}$ are the areas of the emission spectra (normalized by the absorbed photon number at the excitation wavelength, $\lambda_{\text{ex}}$) associated with the Re ring unit in the emission spectra of [Ring-Ru]$_5^{3+}$ and [Ring-Ru]$_5^{3+}$, respectively, and $\epsilon_{\text{Ring}}$ and $\epsilon_{\text{Ru}}$ are the molar absorption coefficients of [Ring]$_3^{3+}$ and [Ru]$_1^{2+}$ at $\lambda_{\text{em}}$ respectively. The emission spectrum of [Ring-Ru]$_5^{3+}$ excited at $\lambda_{\text{ex}} = 380$ nm was deconvoluted using the emission spectra of [Ring]$_3^{3+}$ and [Ru]$_1^{2+}$ to estimate $A_{\text{sim}(\text{Ring-Ru})}$ (Figure 4b). From these analyses, $\eta_{ET}$ in the case of [Ring-Ru]$_5^{3+}$ was estimated to be 78%. Notably, such efficient intramolecular energy transfer is caused by the covalent linkage between the Re ring and the Ru complex units, as confirmed by energy transfer not being observed for an equimolar mixed solution of the model Re ring ([Ring]$_3^{3+}$) and the model Ru mononuclear complex ([Ru]$_1^{2+}$) (Figure S3).

We also investigated this excitation energy-transfer event in [Ring-Ru]$_5^{3+}$ by measuring the emission lifetimes and recording the corresponding transient emission spectra. Figure 6a shows the transient emission spectra of [Ring-Ru]$_5^{3+}$ acquired using the single-photon counting method. In the initial stage, rapid decay was observed at $480 \leq \lambda_{\text{em}} \leq 560$ nm, and an increase of the emission intensity in the longer-wavelength region ($\lambda_{\text{em}} > 570$ nm) was observed in this time.
"Energy-transfer efficiency calculated on the basis of steady-state emission experiments (eq 1). \(^*\) Rate constants of energy transfer calculated according to eq 2 or eqs 4–6. \(^*\) The energy-transfer rate constant from the Re(n) unit to the Ru unit. \(^*\) The energy-transfer rate constant from the Ru unit to the Re(n) unit. \(^*\) The energy-transfer rate constant from the Re(p) unit to the Ru unit. \(^*\) Energy-transfer efficiency calculated on the basis of emission lifetimes (eq 3). \(^*\) Weighted average of \(\eta_{ET1}\) and \(\eta_{ET2}\). \(^*\) The concentration ratio between the excited Ru unit and the excited Re(n) unit in the excited [Ring-Ru3]\(^{5+}\) was approximately 6.7:1 after equilibrium was reached. \(^*\) The efficiency of the intraring energy transfer.

Table 2. Energy-Transfer Rate Constants and Efficiencies in the [Ring-Ru\(^{5+}\)] complexes in degassed MeCN at 25°C

| complex | \(\eta_{ET1}^\text{a} (%)\) | \(k \times 10^7 \text{ s}^{-1}\) | \(\eta_{ET2}^\text{b}\) (%) | \(\eta_{ET1}^\text{a} \times 1/3 \times \eta_{ET2}^\text{b} \times 2/3\) (%) |
|---------|-----------------|-----------------|-----------------|---------------------|
| [Ring-Ru1]\(^{5+}\) | 78 | 62 | 1.4 | 99 |
| [Ring-Ru2]\(^{5+}\) | 95 | 250 | 4.3 | >99 |
| [Ring-Ru3]\(^{5+}\) | 4.0 | 0.56 | 52 | 13 |
| [Ring3]\(^{5+}\) | 98 | - | 7.6 | - |

The weighted average of \(\eta_{ET1}\) and \(\eta_{ET2}\) (eq 2) well matches the value estimated by fitting the emission spectrum of [Ring-Ru1]\(^{5+}\) (78%), as previously described. We reasonably assumed that the node-Re moiety connected with the Ru unit was quenched more efficiently than the other Re moieties with 4dmb because of the direct connection via the ethylene chain and the short distance to the Ru unit. These excitation energy-transfer events of [Ring-Ru\(^{5+}\)] are summarized in Figure 7a.

Figure 7. Energy-transfer processes and their rate constants in (a) [Ring-Ru1]\(^{5+}\) and (b) [Ring-Ru2]\(^{5+}\).

Similar photophysical phenomena were observed in the case of [Ring-Ru\(^{2+}\)] (Figures 5b and 8 and Table 1); that is, the maximum emission wavelengths and the quantum yield (\(\lambda_{em}^\text{max} = 604 \text{ nm, } \Phi_{em} = 6.3\%\)) are similar to those of [Ru2]\(^{2+}\) (\(\lambda_{em}^\text{max} = 604 \text{ nm, } \Phi_{em} = 4.1\%\)) and dramatically different from those of [Ring2]\(^{3+}\) (\(\lambda_{em}^\text{max} = 553 \text{ nm, } \Phi_{em} = 44\%\)). The excitation..."
than that of Ru unit. Because the pre-exponential factor of $\lambda_{1}$ was much larger than that of Ru complex unit with a conjugated vinyl group, was red-shifted and closer to that of $[\text{Ru}^2]^{2+}$ (Figure 10a) compared with $[\text{RingRu}^2]^{2+}$ (sky blue) and spectral deconvolution into individual emissions of $[\text{Ring2}]^{3+}$ (green) and $[\text{Ru2}]^{2+}$ (red) and their sum (black dotted line).

The energy-transfer processes and the emission decay curves could be fitted with a triple-exponential function; the obtained lifetimes were $\tau_1 = 130$ ns, $\tau_2 = 840$ ns, and $\tau_3 = 5$ ns (Figure 11a). The emission decay measured at $\lambda_{\text{det}} = 650$ nm was drastically faster than that at $\lambda_{\text{det}} = 550$ nm (Figure 11b). These results strongly suggest that intramolecular energy transfer proceeded among the Re complex units in the fittings of $[\text{Ring-Ru}^1]^{5+}$ and $[\text{Ring-Ru}^2]^{5+}$.

Before investigating the properties of the excited $[\text{Ring-Ru}^3]^{5+}$, we carefully checked the photophysical behaviors of $[\text{Ring3}]^{3+}$. Notably, this analyzed sample contained a minimal amount of $[\text{Ru}^4]^{2+}$, which could not be removed and was detected as small peaks in the ESI mass spectrum (Figure S4). However, the effects of this impurity on the photophysical properties of the sample are easily corrected for, as described later. The transient emission spectra of $[\text{Ring3}]^{3+}$ show a gradual red-shift of the maximum emission wavelength from $\lambda_{\text{max}} = 605$ nm (5 ns) to $\lambda_{\text{max}} = 635$ nm (1000 ns) (Figure 11a). The emission decay measured at $\lambda_{\text{det}} = 550$ nm was drastically faster than that at $\lambda_{\text{det}} = 650$ nm (Figure 11b). These results strongly suggest that intramolecular energy transfer proceeded among the Re complex units in $[\text{Ring3}]^{3+}$.

The emission decay curves could be fitted with a triple-exponential function; the obtained lifetimes were $\tau_1 = 130$ ns, $\tau_2 = 840$ ns, and $\tau_3 = 5$ $\mu$s, respectively. Because $\tau_3$ was a minor component in the emission, it likely originated from the $[\text{Ring4}]^{2+}$ impurity because $\tau_3$ is very similar to the emission lifetime of $[\text{Ru}^3]^{2+}$ ($\tau_{\text{em}} = 5.4$ $\mu$s). Therefore, the emission lifetimes from $[\text{Ring3}]^{3+}$ itself should be $\tau_1 = 130$ ns and $\tau_2 = 840$ ns for $[\text{Ring-Ru}^3]^{5+}$.

Figure 8. (a) Normalized emission spectra of $[\text{RingRu}^2]^{3+}$ in degassed MeCN measured using excitation light with various wavelengths: $\lambda_{\text{ex}} = 380$ nm (sky blue) and $\lambda_{\text{ex}} = 460$ nm (blue dotted line). The emission spectra of $[\text{Ring2}]^{3+}$ (green) and $[\text{Ru2}]^{2+}$ (red) are also illustrated. (b) Emission spectrum of $[\text{RingRu}^2]^{3+}$ (sky blue) and spectral deconvolution into individual emissions of $[\text{Ring2}]^{3+}$ (green) and $[\text{Ru2}]^{2+}$ (red) and their sum (black dotted line).

Figure 9. (a) Transient emission spectra of $[\text{Ring-Ru}^2]^{5+}$ measured in MeCN with $\lambda_{\text{ex}} = 379$ nm. (b) Emission decay curves of $[\text{Ring-Ru}^2]^{5+}$ recorded at 520 nm (red) and 650 nm (blue).
840 ns. The emission maximum of [Ring4]3+ (Figure 10a), which consists of only the Re complex units with Sdmb, was blue-shifted compared with that of [Ring3]3+ (Figure 10a) and the wavelength dependence of the pre-exponential factors of \( \tau_1 \) of [Ring3]3+ (Figure S5) was similar to the emission spectrum of [Ring4]3+ (yellow green spectrum in Figure 10a). These results strongly suggest that \( \tau_1 \) and \( \tau_2 \) are the emission lifetimes associated with the Re units with Sdmb and that with 4-vinyl-bpy (vbpy), respectively, and that the excitation energy was transferred from the Re units with Sdmb to that with vbpy. The rate constant of the energy transfer in [Ring3]3+ (\( k_{ET} \)) was calculated as \( k_{ET} = 7.6 \times 10^6 \) s\(^{-1}\) using eq 2 with \( \tau_1 \) and the emission lifetime of [Ring4]3+ (\( \tau_{[Ring4]3^+} = 5.4 \) µs, Figure 12a). According to eq 3, the efficiency of this intraring energy transfer was \( \eta_{ET} = 98\% \) (Figure 12a).

Figure 13a shows the transient emission spectra of [Ring-Ru3]5+. The time profiles of the emission in the shorter-wavelength region (<600 nm) show a rapid decrease within 50 ns. This behavior is attributable to energy transfer from the Re units with the Sdmb ligand to other units in [Ring-Ru3]5+.

Notably, this decay rate is much higher than that of the energy transfer from the Re units with the Sdmb ligand to the Re unit with the vbpy ligand in [Ring3]3+. This difference strongly suggests that energy transfers from the Re units with the Sdmb ligand directly to the Ru unit as well (red arrow in Figure 12b). In addition, from 50 to 400 ns, another slower and smaller change in the spectrum shape is observed, i.e., a decrease in the wavelength region <600 nm and an increase at ∼630 nm (Figure 13b); the transient spectrum then monotonically decays without a change in the spectrum shape after 400 ns. This spectrum shape recorded after 800 ns was well-fitted with the emission spectra of [Ru3]2+ and [Ring3]3+ (Figure S6). These results indicate that another energy transfer occurred from the Re unit with the vbpy ligand to the Ru unit in the time interval to 400 ns and that the reverse energy transfer from the Ru unit to the Re unit with the vbpy ligand simultaneously proceeded (green arrows in Figure 12b). These forward and backward energy-transfer processes should arrive at an equilibrium state at 400 ns after the laser irradiation.

Figure 13c shows emission decay curves of [Ring-Ru3]3+ recorded at \( \lambda_{em} = 550 \) and 650 nm as typical examples (\( \lambda_{ex} = 337 \) nm), which could be roughly fitted using a triple-exponential function with \( \tau_1 = 23 \) ns, \( \tau_2 = 140 \) ns, and \( \tau_3 = 980 \) ns. Notably, the pre-exponential functions of \( \tau_1 (A_1) \) and \( \tau_2 (A_2) \) at ∼600 nm were negative values because of the slower energy transfer between 50 and 400 ns after laser irradiation (Figure 13d); in this time region, the ratio between the excited Re unit with the vbpy ligand and the excited Ru unit should be greater than that in the equilibrium state because the Ru unit has a slightly longer emission maximum than the Re unit with the vbpy ligand. This result also suggests that the process with \( \tau_2 = 140 \) ns involves a change in the concentration ratio between the excited Ru unit and the excited Re unit with the vbpy ligand. Because the lifetimes of the excited state of [Ru3]2+ and the Re unit with the vbpy ligand of [Ring3]3+ are similar to each other and also similar to the longest emission lifetime of [Ring-Ru3]3+ (Table 1), the emission with \( \tau_3 = 980 \) ns is attributed...
to both the excited Ru unit and the excited Re unit with the vbpy ligand.

To determine the exact rate constants of energy-transfer processes among the three different units in \([\text{Ring-Ru3}]^{5+}\), i.e., the Ru unit, the Re units with the 5dmb ligand, and the node-Re unit directly connected with the Ru unit, we analyzed the emission decays measured at three different detection wavelengths (550, 575, and 650 nm). These emission decays are mainly associated with the Re units with the 5dmb ligand, a mixture of emissions from all of the units, and the Ru unit, respectively. We conducted the analyses using the rate equations based on the photophysical processes of \([\text{Ring-Ru3}]^{5+}\) (Figure 14).

![Figure 14. Photophysical processes of \([\text{Ring-Ru3}]^{5+}\).](image)

The concentrations of the excited states of \([\text{Ring-Ru3}]^{5+}\) at time \(t\) seconds after excitation are abbreviated as \(A(t)\), \(B(t)\), and \(C(t)\), where the excited units are the Re unit with the 5dmb ligand (Re(p)), the Re unit directly connected to the Ru unit (Re(n)), and the Ru unit itself (Ru), respectively. These concentration changes can be formulated by the following set of rate equations (eqs 4–6):

\[
\frac{dA(t)}{dt} = -(k_1 + k_{ET0} + k_{ET2})A(t)
\]

\[
\frac{dB(t)}{dt} = k_{ET0}A(t) + k_{ET1}C(t) - (k_B + k_{ET1})B(t)
\]

\[
\frac{dC(t)}{dt} = k_{ET2}A(t) + k_{ET1}B(t) - (k_C + k_{ET1})C(t)
\]

The observed emission intensity \(I_{em}(\lambda, t)\) at the monitoring wavelength \(\lambda\) and time \(t\) was calculated using the concentrations of the excited states \(I\). The numerical parameters relate to their emission spectra and the spectral sensitivities of the apparatus as

\[
I_{em}(\lambda, t) = \sum_{J=A,B,C} a(\lambda) b(\lambda) \Phi_J f(J, \lambda, t)
\]

where \(a(\lambda)\) is the apparatus constant of the instrument at wavelength \(\lambda\), \(b(\lambda)\) the numerical constant of the emission spectral shape of the excited species \(J\) at wavelength \(\lambda\), and \(f(J, \lambda, t)\) the concentration of the excited state \(J\).

The set of rate equations was numerically solved, and the emission decays of the \([\text{Ring-Ru3}]^{5+}\) measured at 550, 575, and 650 nm (Figure 15) were analyzed using the nonlinear model fit method in the Wolfram Mathematica 10 software (Wolfram Research Inc.) to minimize the deviation of the evaluated values from those in the emission decay data with the parameters, as previously described; both the precision goal and the accuracy goal were set to \(10^{-8}\), and the experimentally obtained parameters from the measurement of the model species, \([\text{Ring3}]^{3+}\), \([\text{Ring4}]^{3+}\), and \([\text{Ru3}]^{2+}\) (i.e., \(k_1 = 1.9 \times 10^5\) s\(^{-1}\), \(k_B = 1.2 \times 10^6\) s\(^{-1}\), and \(k_C = 1.0 \times 10^6\) s\(^{-1}\)) were used. Reasonable fitting was obtained, as shown in Figure 15. The evaluated kinetic parameters are summarized along with other photophysical parameters in Table 2.

![Figure 15. Emission decay profiles of \([\text{Ring-Ru3}]^{5+}\) monitored at (a) 550, (b) 575, and (c) 650 nm (red dots) with the simulated emission intensities (orange curves) and residuals (red dots). The calculated relative concentration changes of three excited states of \([\text{Ring-Ru3}]^{5+}\) are presented in panel d.](image)

Interestingly, the value of \(k_{ET2}\) of \([\text{Ring-Ru3}]^{5+}\), which is the energy-transfer rate from the excited Re unit with the 5dmb ligand to the Ru unit, is relatively large even though the length of the spacer between the Ru unit and the Re ring unit is the longest among the ring–Ru complexes. This result suggests that the Ru unit can collide with the Re units with 5dmb because of the flexibility of the long bridging chain. The obtained energy-transfer rate from the excited Re unit with the 5dmb ligand to the Re unit directly connected with the Ru unit in \([\text{Ring-Ru3}]^{5+}\) \((k_{ET2} = 13 \times 10^6\) s\(^{-1}\)) is slightly greater than that from the excited Re unit with the 5dmb ligand to the Re unit with the vbpy ligand in \([\text{Ring3}]^{3+}\) \((k_{ET2} = 7.6 \times 10^6\) s\(^{-1}\)). This difference might be caused by different conformations of the Re ring moiety in \([\text{Ring-Ru3}]^{5+}\) and that of \([\text{Ring3}]^{3+}\) because of the steric hindrance of the Ru unit and flexibility of the bridging bispophine ligands, i.e., dppe. The rate constant of forward energy transfer from the Ru unit to the Re unit, each of which is directly connected, was \(k_{ET1} = 4.0 \times 10^6\) s\(^{-1}\), and that of the backward energy transfer was \(k_{ET1} = 0.56 \times 10^6\) s\(^{-1}\); therefore, the concentration ratio between the excited
Ru unit and the excited Re(n) unit in the excited [Ring-Ru3]5+ was approximately 6.7:1 after equilibrium was established between them.

**CONCLUSIONS**

We developed two efficient synthetic strategies to construct covalently linked trinuclear Re(I) rings with the Ru(II)-trisdiimine mononuclear complex [Ring-Ru]5+(n = 1, 2, 3). These complexes exhibit strong absorption in the visible region because of the efficient intramolecular energy transfer among the Re units and between the Re ring and the Ru unit. Notably, both the Re rings and [Ru(diimine)]2+ complexes function as excellent redox photosensitizers (photoredox catalysts), and [Ring-Ru]5+ has both complex units. Therefore, this multinuclear complex can potentially function as good redox photosensitizers with stronger visible-light absorption than the Re rings and [Ru(diimine)]2+ complexes. The synthesis methods of [Ring-Ru]5+ should enable any diimine-coordinating metal complexes to be tethered to the Re ring, leading to the construction of novel Re rings with various metal complexes.

**EXPERIMENTAL SECTION**

Materials and Methods

Acetonitrile was dried over P2O5 three times and then distilled from CaH2 prior to use. Other anhydrous solvents were purchased from commercial sources. All reactions were carried out under an inert atmosphere and in dim light. Column chromatography was performed with Silica Gel 60 (40–50 μm, Kanto Chemical Co.), alumina (standardized, Merck), or Sephadex (GE Healthcare). 2,2′-Bipyridine (bp), 4,4′-dimethyl-2,2′-bipyridine (4db), 5,5′-dimethyl-2,2′-bipyridine (5db), 1,2-bis(diphenylphosphino)ethane (dppe), Re(CO)5Br, RuCl3, MeCN, EtOH, or MeNO2, and other commercially available reagents were purchased from Kanto Chemical Co., Tokyo Kasei Co., Wako Pure Chemical Industries, and Aldrich Chemical Co. and were used as received. Syntheses of 4′-but-3-ethyl-4,4′-bipyridyl (allyl-4db), 1,2-bis(4′-methyl-2,2′-bipyridinyl-4-yl)ethane (4C2), and analogously 1,2-bis(5′-methyl-2,2′-bipyridinyl-5-yl)ethane (5C2), p-bis(diphenylphosphino)benzene (dppph), and Re(CO)Br were reported elsewhere. The 4-(2-hydroxethyl)-2,2′-bipyridine (OHbp)2, fac-Re(N=N)(CO)Br-type, fac-Re(N=N)(CO)OTf-type, Ru(N=N)Cl-type, and dinuclear Re(1) complexes ([L2xx(–N=N)]4+, xx = bisphosphine ligand) were synthesized according to the reported methods with some modifications and using corresponding N=N ligands. Syntheses of the trinuclear ring complexes [R3ph(N=N)]5− and [R4et(5dbbBrbpy)]5− were published recently. All target complexes were obtained as PF6− salts.

Photophysical reactions were performed with a 500 W high-pressure Hg lamp EHBWI (Eikosha) with a uranium glass filter (>330 nm) in a Pyrex squat-tub-form cell, with bubbling of N2 gas. During irradiation, both the reaction vessel and the light source were cooled with tap water. Separation of larger complexes was achieved by RSEC using a pair of Shodex PROTEIN KW-2002.5 columns (300 mm x 20.0 mm i.d.) with a KL-LG guard column (50 mm x 8.0 mm i.d.) and a JAIC LC-9201 recycling preparative HPLC apparatus (Japan Analytical Industry Co.) with a JASCO 870-UV detector (the detection wavelength was chosen as 360 nm); the eluent was MeOH–MeCN (1:1 v/v) containing CH3COONH4 (0.15 M), and the flow rate was 6.0 mL min−1. For analytical SEC, two sequentially connected Shodex KW-402.5-4F columns (300 mm x 4.6 mm i.d.) were used, with a KW400G-4A guard-column (10 mm x 4.6 mm i.d.), a JASCO 880-51 degasser, an 880-PU pump, an MD-2010 Plus UV–Vis photodiode-array detector (λex = 360 nm), and a Rheodyne 7125 injector. The column temperature was maintained at 40 °C using a JASCO 860-C0 column oven. The eluent was MeOH–MeCN (1:1 v/v) containing CH3COONH4 (0.5 M), and the flow rate was 0.2 mL min−1. 1H NMR and 31P NMR spectra were acquired with a JEOL ECA400II spectrometer. Chemical shifts (δ/ppm) were referenced to the residual 1H signals of a deuterated solvent (1.94 ppm for CDCl3 and 2.05 ppm for CD3OD), and the 31P signal of PF6− (−14 ppm), respectively. All NMR spectra were recorded at room temperature. ESI mass spectrometry (ESI-MS) was conducted on a Shimadzu LCMS-2010A mass spectrometer. ESI time-of-flight mass spectrometry was undertaken with a Waters LCT Premier instrument. Fourier transform infrared (FT-IR) spectra were recorded with a JASCO FT/IR-610 spectrometer at 1 cm−1 resolution with a TGS detector.

UV–Vis absorption spectra were recorded with a JASCO V-565 or V-670 spectrophotometer. Emission spectra were recorded at 293 °C using a JASCO FP-6500 spectrofluorometer and were corrected for photomultiplier tube response. Emission quantum yields were determined with a calibrated integrating sphere (Absolute PL Quantum Yield Measurement System C9920-01, Hamamatsu Photonics k.k.) comprising a Xe lamp as an excitation source and a multichannel spectrometer (C10027). Emission lifetimes were measured at 25 °C using a HORIBA FluoroCube time-correlated single-photon counting system. The excitation light source was a NanoLED-560 (379 nm, <200 ps; 401 nm, <200 ps; 456 nm, <1.3 ns, or 510 nm, <100 ps). All measurements were performed in a quartz cubic cell (1 cm optical path length). The absorbances were adjusted to 0.1 at λem, otherwise, the photoluminescence responses were corrected to the number of absorbed photons in the case of using various excitation wavelengths of a single solution. Prior to measurements, the solutions were degassed using the pump–thaw–freeze method.

**Syntheses**

### Synthesis of [Ring-Ru1]5+. [Ru(bpy)2(4C2)][PF6]2, Ru(bpy)2Cl2, H2O (150 mg, 0.29 mmol) and 4C2 (420 mg, 1.16 mmol) were refluxed in MeOH (25 mL) overnight. The solvent was evaporated, and the resultant crude product was dissolved in H2O (30 mL) and filtered to remove the excess of 4C2. Solid NH4PF6 (excess) was added to the filtrate; extraction was performed with CH2Cl2 (2 × 50 mL), and the combined organic layers were evaporated to dryness. The crude solid was purified by column chromatography (alumina, CH2Cl2 and MeCN–CH2Cl2 8:1), yielding 280 mg of a red solid (90%). ESI-MS (CH3CN): m/z 389 [M–2PF6]−.

### Synthesis of [Ring-Ru2]5+. [Ru(bpy)2(4C2)][PF6]2, Ru(bpy)2Cl2, H2O (150 mg, 0.29 mmol) and 4C2 (420 mg, 1.16 mmol) were refluxed in MeOH (25 mL) overnight. The solvent was evaporated, and the resultant crude product was dissolved in H2O (30 mL) and filtered through a pad of silica gel. ESI-MS: m/z 389 [M–2PF6]−.

### Synthesis of [Ring-Ru3]5+. [Ru(bpy)2(4C2)][PF6]2, Ru(bpy)2Cl2, H2O (150 mg, 0.29 mmol) and 4C2 (420 mg, 1.16 mmol) were refluxed in MeOH (25 mL) overnight. The solvent was evaporated, and the resultant crude product was filtered to remove the excess dppph, and the precipitate was filtered through a pad of silica gel. ESI-MS: m/z 389 [M–2PF6]−.

### Synthesis of [Ring-Ru4]5+. [Ru(bpy)2(4C2)][PF6]2, Ru(bpy)2Cl2, H2O (150 mg, 0.29 mmol) and 4C2 (420 mg, 1.16 mmol) were refluxed in MeOH (25 mL) overnight. The solvent was evaporated, and the resultant crude product was dissolved in H2O (30 mL) and filtered through a pad of silica gel. ESI-MS: m/z 389 [M–2PF6]−.

### Synthesis of [Ring-Ru5]5+. [Ru(bpy)2(4C2)][PF6]2, Ru(bpy)2Cl2, H2O (150 mg, 0.29 mmol) and 4C2 (420 mg, 1.16 mmol) were refluxed in MeOH (25 mL) overnight. The solvent was evaporated, and the resultant crude product was dissolved in H2O (30 mL) and filtered through a pad of silica gel. ESI-MS: m/z 389 [M–2PF6]−.
irradiated in degassed CH₂Cl₂ (150 mL) for 35 min. After evaporation of the solvent, the crude red solid was dissolved in CH₂Cl₂ (25 mL) together with the crude fac-[Re(CO)₃(η⁶-dppphp)-(μ-4C₂)Ru(bpy)]⁺ from the previous step and the solution was stirred at room temperature (rt) for 3 days. The solvent was evaporated, and the crude material was purified by RSEC. The fractions corresponding to the product were collected, evaporated, and partitioned between CH₂Cl₂ and NH₄PF₆ aqueous solution. The organic layer was washed once more with aqueous NH₄PF₆ solution, dried over Na₂SO₄, and evaporated to yield 60 mg of red crystals (28%, based on [L2p(4mdb)][3]). ¹³P NMR (161 MHz, CDCl₃): δ 22.6, 21.5, 17.6, 17.3 ppm. FT-IR (CHCl₃): νCO 2040, 1954, 1939, 1924, 1869 cm⁻¹. ESI-MS (CH₂CN): m/z 965 [M−5PF₆]⁻, 774 [M−4PF₆]⁻, 672 [M−3PF₆]⁻, 571 [M−2PF₆]⁻, 470 m/z. Evaporation of the solvent, the crude red solid was dissolved in CH₂Cl₂ (30 mL) together with the crude fac-[Re(CO)₃(η⁶-dppphp)-(μ-4C₂)Ru(C₂)Ru(bpy)]⁺ from the previous step, and the resultant solution was stirred at rt for 3 days. The solvent was evaporated, and the crude material was purified using RSEC. The fraction containing the product was collected, evaporated, and partitioned between dppph and NH₄PF₆ aqueous solution. The organic layer was washed once more with aqueous NH₄PF₆ solution, dried over Na₂SO₄, and evaporated to yield 43 mg of dark orange crystals (16%, based on [L2p(4mdb)][3]). ESI-MS (CH₂CN): m/z 576 [M−5PF₆]⁻, 757 [M−4PF₆]⁻, 673 [M−3PF₆]⁻, 578 [M−2PF₆]⁻, 470 m/z. Evaporation of the solvent, the crude red solid was dissolved in CH₂Cl₂ (30 mL) together with the crude fac-[Re(CO)₃(η⁶-dppphp)-(μ-4C₂)Ru(C₂)Ru(bpy)]⁺ from the previous step, and the resultant solution was stirred at rt for 1 h. The solvent was evaporated, and the crude material was purified using RSEC. The fraction containing the product was collected, evaporated, and partitioned between CH₂Cl₂ and NH₄PF₆ aqueous solution. The organic layer was washed once more with aqueous NH₄PF₆ solution, dried over Na₂SO₄, and evaporated to yield 43 mg of dark orange crystals (16%, based on [L2p(4mdb)][3]). ESI-MS (CH₂CN): m/z 576 [M−5PF₆]⁻, 757 [M−4PF₆]⁻, 673 [M−3PF₆]⁻, 578 [M−2PF₆]⁻, 470 m/z. Evaporation of the solvent, the crude red solid was dissolved in CH₂Cl₂ (30 mL) together with the crude fac-[Re(CO)₃(η⁶-dppphp)-(μ-4C₂)Ru(C₂)Ru(bpy)]⁺ from the previous step, and the resultant solution was stirred at rt for 3 days. The solvent was evaporated, and the crude material was purified using RSEC. The fraction containing the product was collected, evaporated, and partitioned between CH₂Cl₂ and NH₄PF₆ aqueous solution. The organic layer was washed once more with aqueous NH₄PF₆ solution, dried over Na₂SO₄, and evaporated to yield 43 mg of dark orange crystals (16%, based on [L2p(4mdb)][3]). ESI-MS (CH₂CN): m/z 576 [M−5PF₆]⁻, 757 [M−4PF₆]⁻, 673 [M−3PF₆]⁻, 578 [M−2PF₆]⁻, 470 m/z. Evaporation of the solvent, the crude red solid was dissolved in CH₂Cl₂ (30 mL) together with the crude fac-[Re(CO)₃(η⁶-dppphp)-(μ-4C₂)Ru(C₂)Ru(bpy)]⁺ from the previous step, and the resultant solution was stirred at rt for 3 days. The solvent was evaporated, and the crude material was purified using RSEC. The fraction containing the product was collected, evaporated, and partitioned between CH₂Cl₂ and NH₄PF₆ aqueous solution. The organic layer was washed once more with aqueous NH₄PF₆ solution, dried over Na₂SO₄, and evaporated to yield 43 mg of dark orange crystals (16%, based on [L2p(4mdb)][3]). ESI-MS (CH₂CN): m/z 576 [M−5PF₆]⁻, 757 [M−4PF₆]⁻, 673 [M−3PF₆]⁻, 578 [M−2PF₆]⁻, 470 m/z. Evaporation of the solvent, the crude red solid was dissolved in CH₂Cl₂ (30 mL) together with the crude fac-[Re(CO)₃(η⁶-dppphp)-(μ-4C₂)Ru(C₂)Ru(bpy)]⁺ from the previous step, and the resultant solution was stirred at rt for 3 days. The solvent was evaporated, and the crude material was purified using RSEC. The fraction containing the product was collected, evaporated, and partitioned between CH₂Cl₂ and NH₄PF₆ aqueous solution. The organic layer was washed once more with aqueous NH₄PF₆ solution, dried over Na₂SO₄, and evaporated to yield 43 mg of dark orange crystals (16%, based on [L2p(4mdb)][3]). ESI-MS (CH₂CN): m/z 576 [M−5PF₆]⁻, 757 [M−4PF₆]⁻, 673 [M−3PF₆]⁻, 578 [M−2PF₆]⁻, 470 m/z. Evaporation of the solvent, the crude red solid was dissolved in CH₂Cl₂ (30 mL) together with the crude fac-[Re(CO)₃(η⁶-dppphp)-(μ-4C₂)Ru(C₂)Ru(bpy)]⁺ from the previous step, and the resultant solution was stirred at rt for 3 days. The solvent was evaporated, and the crude material was purified using RSEC. The fraction containing the product was collected, evaporated, and partitioned between CH₂Cl₂ and NH₄PF₆ aqueous solution. The organic layer was washed once more with aqueous NH₄PF₆ solution, dried over Na₂SO₄, and evaporated to yield 43 mg of dark orange crystals (16%, based on [L2p(4mdb)][3]). ESI-MS (CH₂CN): m/z 576 [M−5PF₆]⁻, 757 [M−4PF₆]⁻, 673 [M−3PF₆]⁻, 578 [M−2PF₆]⁻, 470 m/z. Evaporation of the solvent, the crude red solid was dissolved in CH₂Cl₂ (30 mL) together with the crude fac-[Re(CO)₃(η⁶-dppphp)-(μ-4C₂)Ru(C₂)Ru(bpy)]⁺ from the previous step, and the resultant solution was stirred at rt for 3 days. The solvent was evaporated, and the crude material was purified using RSEC. The fraction containing the product was collected, evaporated, and partitioned between CH₂Cl₂ and NH₄PF₆ aqueous solution. The organic layer was washed once more with aqueous NH₄PF₆ solution, dried over Na₂SO₄, and evaporated to yield 43 mg of dark orange crystals (16%, based on [L2p(4mdb)][3]). ESI-MS (CH₂CN): m/z 576 [M−5PF₆]⁻, 757 [M−4PF₆]⁻, 673 [M−3PF₆]⁻, 578 [M−2PF₆]⁻, 470 m/z.
MeOH was evaporated under reduced pressure. After product precipitation, an orange-red solid was collected, washed with water and EtO₂, and dried under vacuum to yield 5.2 mg (40%) of product. ¹H NMR (400 MHz, acetone-d₆): δ 8.74 (s, 2H), 8.67 (d, J = 6.8 Hz, 1H), 8.64 (m, 3H), 8.61 (s, 2H), 8.38 (s, 2H), 8.21 (s, 2H), 7.96-7.78 (m, 17H), 7.64-7.58 (m, 6H), 7.39-7.11 (m, 40H), 7.03-6.82 (m, 20H), 6.61 (m, 1H), 6.57 (m, 1H), 2.98-2.87 (m, 12H, P-CH₂-CH₂-P), 2.55-2.51 (m, 19H, = CH₂-CH₂-CH = (CH₂-4dbmb-CH₂), 2.18 (s, 6H, 5dmb-CH₃), 2.14 (s, 6H, Sdbm-CH₃) ppm. ³¹P NMR (161 MHz, acetone-d₆): δ 13.4 (4P), 13.2 (2P) ppm. FT-IR (CH₃CN): δ 2,87 (m, 12H, P), 2.18 (s, 6H, 5dmb-C₃), 1.85 (s, 12H, 5dmb-CH₂), 1.59 (s, 36H, 5dmb), 1.38 (s, 12H, 5dmb), 1.07 (s, 36H, 5dmb) ppm.

**Synthesis of [Ring₃]⁺.** fac-[Re(OHbpy)(CO)₂][PF₆] (101 mg, 0.12 mmol) in degassed CH₂Cl₂ was irradiated for 30 min. After evaporation of the solvent, the residue was re-dissolved in CH₂Cl₂ and twice washed with Et₂O, and dried under vacuum to yield a yellow solid. Some degassed MeOH solution of NH₄PF₆ was added. Some water was added to the MeOH solution of NH₄PF₆ and evaporated, and the resultant mixture was re-evaporated for 20 h. The solvent was removed under reduced pressure. After product precipitation, a yellow solid was collected, washed with water containing NH₄PF₆. After evaporation of the organic layer, the resultant mixture was re-evaporated for 1 d. After the solution cooled to rt, the solvent was removed under reduced pressure, and the orange-red residue was redissolved in degassed CH₂Cl₂ (50 mL) and filtered. The combined MeOH solutions were evaporated, and the resultant crude product was purified twice by column chromatography with different eluents (silica gel, CH₂Cl₂ and MeOH) and Et₂O, and dried under vacuum to a brown solid. The crude reaction mixture after Mizoroki–Heck cyclization of [L3(4dbmb)-Ru(4dbmb, bpy)₂]⁺ with dpdpb; SEC chromatogram of the crude reaction mixture after Mizoroki–Heck cyclization of [L3(4dbmb)-Ru(4dbmb, bpy)₂]⁺ recorded after 800 ns of excitation and stimulation spectra; electrochemical properties of model complexes (PDF)

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.0c00114.

**Synthetic scheme of [Ring-Ru₂]³⁺, [R3et-(5dmb, Brbpy)]³⁺, and [Ring₃]³⁺; ESI-MS spectra of the reaction solution for decarbonylation of [L3(4dbmb)-(trans-CO)₂-Ru(4dbmb,bpy)₂]⁺ before and after addition of MeNO; SEC chromatogram of the reaction solution after cyclization of [L3(4dbmb)-Ru(4dbmb,bpy)₂]⁺ with dpdpb; SEC chromatogram of the crude reaction mixture after Mizoroki–Heck heterocoupling; emission spectrum of 1:1 mixture of [Ring1]³⁺ and [Ring2]³⁺; ESI-mass spectrum of a reaction solution before the dehydration reaction containing [−{Re(5dmb)(CO)₂(µ₂-dppet)}₂Re(OHbpy)₂(CO)₂(µ₂-dppet)]⁻(PF₆)₃; wavelength dependence of the pre-exponential factors observed in [Ring-Ru₃]⁺; transient emission spectrum of [Ring-Ru₃]⁺ recorded after 800 ns of excitation and stimulation spectra; electrochemical properties of model complexes

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**Notes**

The authors declare no competing financial interest.

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