

Ring-Shaped Re(I) Multinuclear Complexes with Unique Photofunctional Properties

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Supporting Information

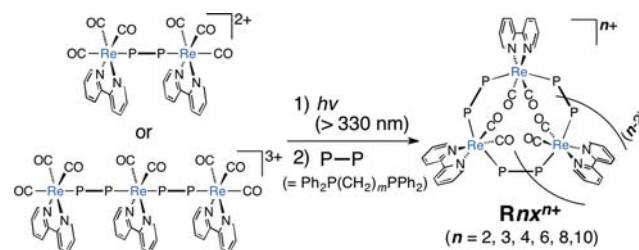
ABSTRACT: We synthesized for the first time a series of emissive ring-shaped Re(I) complexes (Re-rings) with various numbers of Re(I) units and various lengths of bridge ligands. The photophysical properties of the Re-rings could be varied widely through changes in the size of the central cavity. A smaller central cavity of the Re-rings induced intramolecular π - π interactions between the ligands and consequently caused a stronger emission and a longer lifetime of the excited state. The Re-rings can function as efficient and durable photosensitizers. The combination of a trinuclear Re-ring photosensitizer with *fac*-[Re(bpy)(CO)₃(MeCN)]⁺ (bpy = 2,2'-bipyridine) as a catalyst photocatalyzed CO₂ reduction with the highest quantum yield of 82%.

In the photosynthesis of purple bacteria, many chlorophylls are assembled to make the ring-shaped photon-antenna known as LH2.¹ The photon migrates between the chlorophylls in the LH2 and is accumulated in LH1.² Ring-shaped oligomers of Zn porphyrins were reported as the models of the antenna,^{3–6} and energy-hopping phenomena in these porphyrin rings have been intensively investigated.^{6–9} However, these systems have not been used as photosensitizers or photocatalysts. On the other hand, some kinds of transition metal complexes, including Ru(II), Re(I), Os(II), and Ir(III) complexes, have useful photofunctional properties, such as strong absorption of visible light, efficient emission, and long excited-state lifetimes; therefore, they have been tremendously interesting not only from the viewpoint of basic science but also with respect to their various applications, such as in electroluminescence devices and dye-sensitized solar cells.^{10,11} Although some accumulation systems of photofunctional transition metal complexes such as dendrimers and linear- or square-shaped oligomers have been reported,^{12–21} the ring-shaped multinuclear complex has not been reported thus far. We herein report the first systematical synthetic method of various emissive ring-shaped Re(I) diimine multinuclear complexes (Re-rings); we also report our investigation of

their unique photophysical properties, which are very different from those of the corresponding mononuclear complexes, and outstanding reactivities as photosensitizers.

Ring-shaped multinuclear Re(I) complexes were synthesized from dinuclear or trinuclear Re(I) complexes bridged with bidentate phosphine ligands, as shown in Scheme 1, where the

Scheme 1. Synthetic Scheme of R_nxⁿ⁺ [P–P Denotes the Bidentate Phosphine Ligands, Ph₂P(CH₂)_mPPh₂ (m = 2–6)]



Re-rings are abbreviated by R_nxⁿ⁺, where *n* and *x* represent the number of Re(I) centers and an aliphatic chain in the bridge phosphine ligand P–P (Ph₂P(CH₂)_mPPh₂; **e**, *m* = 2; **pr**, *m* = 3; **b**, *m* = 4; **pe**, *m* = 5; **h**, *m* = 6), respectively. As a typical example of the total synthesis, the dinuclear Re(I) complex with 1,2-bis(diphenylphosphino)propane as a bridge ligand, was obtained from the corresponding monomer complex with a labile ligand in 92% yield.¹⁴ The two terminal carbonyl ligands at the *trans*-positions of the phosphine ligand were readily substituted by the solvent molecule upon photoirradiation for several hours.²² Treatment of the produced dinuclear Re(I) complex, whose “solvent” ligands can be easily substituted, with the same bidentate phosphine ligands gave a series of Re-rings, i.e., tetranuclear (R₄pr⁴⁺, 21%), hexanuclear (R₆pr⁶⁺, 8%), octanuclear (R₈pr⁸⁺, 3%), and decanuclear (R₁₀pr¹⁰⁺, 1%) complexes, each of which were isolated using size-exclusion chromatography (SEC).²³ Although larger Re-rings were also detected via analytical SEC and electrospray ionization mass

Received: June 18, 2013

Published: August 22, 2013

spectrometry, they could not be isolated because of the low yields. The Re-rings with different aliphatic chains from $\text{Ph}_2\text{P}(\text{CH}_2)_m\text{PPh}_2$ ($m = 2-6$) were synthesized using a similar method (Figure 1). Table 1 summarizes their isolated yields.

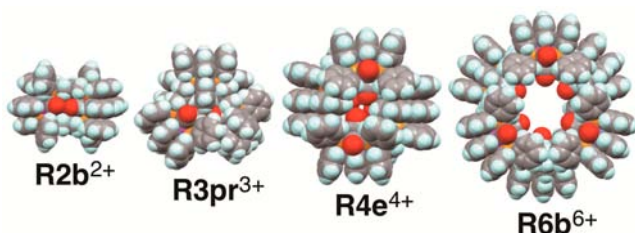


Figure 1. CPK models of the X-ray structures of the Re-rings, R2b^{2+} , R3pr^{3+} , R4e^{4+} , and R6b^{6+} . Gray, light blue, blue, red, orange, and purple spheres represent C, H, N, O, P, and Re atoms, respectively.

Table 1. Isolated Yields of Re-Rings $\text{R}n\text{x}^{n+}$

x	m	R2x^{2+}	R4x^{4+}	R6x^{6+}	R8x^{8+}	R10x^{10+}	R3x^{3+}
e	2	—	17	8	—	—	19
pr	3	—	21	8	3	1	8
b	4	49	17	6	3	—	43
pe	5	38	2	—	—	—	62
h	6	36	5	—	—	—	66

The ring-shaped dinuclear complexes with long aliphatic chains ($m = 4-6$), i.e., R2b^{2+} , R2pe^{2+} , and R2h^{2+} , were produced as main products, whereas the yields of the Re-rings with a larger number of Re(I) units became major products without the formation of the corresponding ring-shaped dinuclear complex in the case of $m = 2$ and 3. On the other hand, the ring-shaped trinuclear Re(I) complexes have been prepared from the corresponding linear trinuclear Re(I) complexes.¹⁴ The larger Re-rings, such as the hexanuclear complex, also formed; however, the yields were too low for the products to be isolated.

The structures of all the rings were characterized using MS, NMR, IR, and elemental analyses, and some of the Re-rings were also characterized using X-ray diffraction analyses (Figure 1, Figures S1–S4, and Tables S1–S5). The X-ray structures of R2b^{2+} , R3pr^{3+} , and R4e^{4+} showed that the diimine and phosphine ligands are closely packed and that both the bpy ligands and the Ph groups of the phosphine ligands are located on the periphery of the ring. On the other hand, the hexanuclear complex (R6b^{6+}) contains a large inner space with a diameter of ~ 6 Å and should therefore have a more flexible structure.

Interestingly, the photophysical properties of the Re-rings varied with both the number of Re(I) units and the length of bridge ligands (Figure S5, Table S6). The Re-rings without a wide cavity in the central space, such as R2b^{2+} , R3pr^{3+} , and R4e^{4+} (Figure 1), all of which contain a small number of Re(I) units and/or bisphosphine ligands with a short alkyl chain, emitted much more strongly than did the corresponding mononuclear complex and linear Re-oligomers; in contrast, the other Re-rings, such as R6b^{6+} , exhibited photophysical properties similar to those of the models. As an example, Figure 2a shows the emission spectra of the Re-rings with 1,2-bis(diphenylphosphino)butane ($\text{R}n\text{b}^{n+}$, $n = 2, 3, 4,$ and 6) along with those of the corresponding Re(I) mononuclear complex (*cis,trans*-[Re(bpy)(CO)₂(PPh₂Et)₂]⁺: M^+) and the linear dinuclear complex ([PPh₂Et(CO)₂(bpy)Re–Ph₂P–

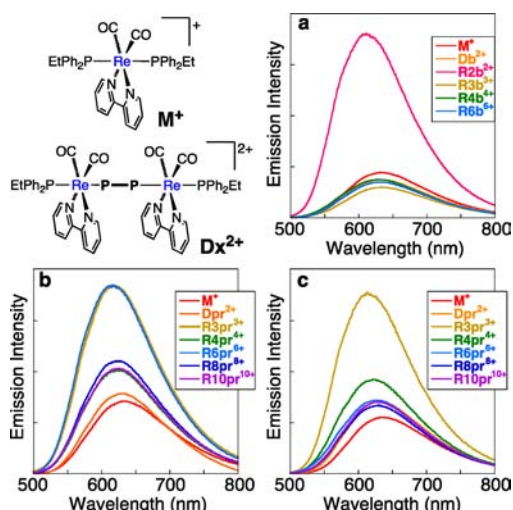


Figure 2. Structures of M^+ and Dx^{2+} , and emission spectra of $\text{R}n\text{b}^{n+}$ ($n = 2, 3, 4,$ and 6) with the model complexes M^+ and $\text{D}b^{2+}$ in CH_3CN (a), and $\text{R}n\text{pr}^{n+}$, M^+ , and $\text{D}pr^{2+}$ ($n = 3, 4, 6, 8,$ and 10) in CH_3CN (b) and in CH_2Cl_2 (c). Emission spectra were normalized to the absorbance at the excitation wavelength (400 nm).

(CH_2)₄PPh₂–Re(bpy)(CO)₂(PPh₂Et)]²⁺: $\text{D}b^{2+}$) in CH_3CN (their structures are shown in Figure 2). The emission quantum yield of R2b^{2+} ($\Phi_{\text{em}} = 0.081$) was ~ 5 times greater and its emission maximum was blue-shifted by ~ 20 nm compared with the corresponding quantities for the other complexes. In the case of the Re-rings with 1,2-bis(diphenylphosphino)propane ($\text{R}n\text{pr}^{n+}$, $n = 3, 4, 6, 8,$ and 10), the emission behaviors were highly dependent on the ring size (Figures 2b). The complexes R4pr^{4+} , R8pr^{8+} , and R10pr^{10+} exhibited emissions at ~ 625 nm ($\Phi_{\text{em}} = 0.028-0.029$) that were ~ 1.5 times more intense than those exhibited by the model complexes ($\Phi_{\text{em}} = 0.018$ (M^+) and 0.020 ($\text{D}pr^{2+}$)) in CH_3CN ; R3pr^{3+} and R6pr^{6+} emitted more strongly at ~ 617 nm by a factor of 2.5 ($\Phi_{\text{em}} = 0.048$), and these emissions were blue-shifted by $\sim 10-20$ nm compared with the emissions of the model complexes (~ 630 nm). Interestingly, although R3pr^{3+} and R4pr^{4+} retained their emission abilities in a less-polar solvent, CH_2Cl_2 , the emission quantum yields of R6pr^{6+} , R8pr^{8+} , and R10pr^{10+} became comparable to those of the model complexes (Figure 2c, Table S6).

The lifetime of the emissive ³MLCT excited state was also strongly affected by the cyclization of the Re(I) complexes. Although emission from the ³MLCT excited state of both the model complexes and the ring-shaped complexes could be analyzed using a double exponential function, which showed lifetimes of ~ 200 and 500–600 ns, respectively (Table S6), the proportion of the longer-lifetime component was significantly greater than that of the shorter-lifetime component in the case of the Re-rings that emitted more strongly than the model complexes. For example, in the cases of $\text{R}n\text{pr}^{n+}$, the most emissive complexes, R3pr^{3+} and R6pr^{6+} , showed a larger proportion of longer lifetimes in CH_3CN (lifetimes: 572 and 593 ns, ratios: 90% and 83%, respectively), which contrasts sharply with the lifetimes of the other Re-rings (lifetimes, 491 and 443 ns, ratios, 44% and 52% for R4pr^{4+} and R8pr^{8+} , respectively) and the model complexes (lifetimes, 474 and 507 ns, ratios, 20% and 29% for M^+ and $\text{D}pr^{2+}$, respectively). However, although this ratio between the longer and shorter lifetimes of R3pr^{3+} was almost maintained in a CH_2Cl_2

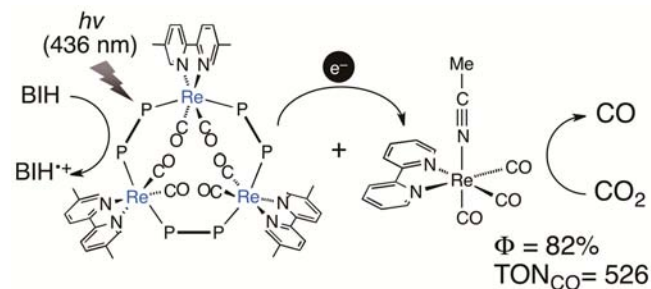
solution, the longer-lifetime proportion decreased to 30% in the case of **R6pr**⁶⁺.

We have already reported that dual emission with different lifetimes was observed from the mononuclear Re(I) complexes with two phosphine ligands, each of which has two phenyl and one alkyl groups, i.e., *cis,trans*-[Re(4,4'-Me₂bpy)-(CO)₂(PPh₂R)₂]⁺.²⁴ Different rotational conformers of such complexes exist because of the rotational motion of the phosphine ligands, which, in turn, determines the extent of the π - π interactions between the aromatic diimine ligand and the phenyl groups on the phosphine ligands. These π - π interactions strongly affected the photophysical properties of the complexes: the lifetime of the excited state became longer, and the Stokes shift between the ¹MLCT absorption band and the emission from the corresponding ³MLCT excited state became smaller.²⁵ On the basis of both the photophysical data (Table S6) and the crystal structures of the Re-rings (Figure 1), one can conclude that the strength of the π - π interaction between the diimine ligand and the phenyl groups of the bisphosphine ligands is controlled by the size of the cavity in the central space. This conclusion is reasonable because, in the case of Re-rings with small cavities, such as **R2b**²⁺, **R3pr**³⁺, and **R4e**⁴⁺, both the diimine ligands and phenyl groups of the bisphosphine ligands should be localized at the outside of their small central cavity, and the rotational motion along the Re-P bond should be limited. This effect is also evident from the intricate IR bands of such Re-rings. The IR spectra displayed the different intensities of the symmetric and the unsymmetric stretching modes depending on the ring size; particularly, **R3pr**³⁺ showed multiple peaks of the latter (Figure S6). It clearly indicated the presence of some stable conformers, even in solution.²⁴ However, the Re-rings with a relatively large cavity showed only two ν_{CO} IR bands, which were attributed to symmetrical and unsymmetrical vibrational bands of the two CO ligands. As described above, **R6pr**⁶⁺ and **R8pr**⁸⁺ were exceptions: although the sizes of their central cavities are large, their emission was stronger, and the proportion of the longer-lifetime component was larger than those of the model complexes and that of the smaller **R4pr**⁴⁺, but only in an MeCN solution. This result is probably because interunit π - π interactions among the aromatic groups of these Re-rings stabilize some favorable conformers for the π - π interactions between the diimine ligand and the phenyl groups of the bisphosphine ligands. Therefore, the emission properties of **R6pr**⁶⁺ and **R8pr**⁸⁺ were similar to those of the models in the less polar solvent, CH₂Cl₂, which should weaken the π - π interactions.

As previously described, the Re-rings that induce the strong π - π interactions have properties that favor the complex functioning as a redox photosensitizer, i.e., strong absorption in the visible region, and a long lifetime of the stable excited state. Therefore, some Re-rings were applied as a photosensitizer with *fac*-[Re(bpy)(CO)₃(MeCN)]⁺ (**Re-MeCN**⁺) as a catalyst for CO₂ reduction. The Re-ring with 5,5'-dimethyl-2,2'-bipyridine ligand (**S-dmb**), i.e., **R3e(S-dmb)**³⁺ ($\tau_{\text{em}} = 5.4 \mu\text{s}$, other data of the Re-ring were shown in Figure S7) produced the best result, probably because these substituents should enhance the reducing power of the corresponding reduced form of the Re-rings.^{26,27} In a typical run, a DMF-TEOA (5:1 v/v) mixed solution that contained **R3e(S-dmb)**³⁺ (0.05 mM), **Re-MeCN**⁺ (0.05 mM), and 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH, 0.03 M)²⁸ as a reductant was irradiated at 436 nm under a CO₂ atmosphere

to achieve the catalytic formation of CO with very small amounts of H₂ and HCOOH (Scheme 2, Figure S8). The

Scheme 2. Highly Efficient Photocatalytic CO₂ Reduction System Composed of a Photosensitizer, **R3e(S-dmb)³⁺ [P-P = Ph₂P(CH₂)₂PPh₂], and a Catalyst, **Re-MeCN**⁺**



quantum yield of CO production (Φ_{CO}) was 82%, and the turnover number (TON_{CO}) was as high as 526.²⁹ It should be noted that this is the most efficient photocatalytic system for CO₂ reduction reported to now and the photocatalytic system with **R3e(S-dmb)**³⁺ can strongly and widely utilize visible light; however the previous most efficient photocatalytic system ($\Phi_{\text{CO}} = 59\%$) that used *fac*-[Re(4-MeObpy)(CO)₃{P(OEt)₃}]⁺ as a photosensitizer and **Re-MeCN**⁺ as catalyst cannot utilize visible light.²⁶

In conclusion, we successfully synthesized a series of the emissive Re-rings with various number of the Re(I) units and various length of the bridge ligands. The photophysical properties of the Re-rings can be widely controlled by changing the size of the central cavity. The Re-rings can work as an efficient and durable photosensitizer for CO₂ reduction to CO in the presence of both a catalyst and the sacrificial electron donor. A combination of **R3e(S-dmb)**³⁺ as a photosensitizer with **Re-MeCN**⁺ as a catalyst photocatalyzed CO₂ reduction with the highest quantum yield of 82%. Further studies on the photocatalytic reactions are now in progress.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details and crystallographic, photophysical, and photocatalytic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially supported by MEXT KAKENHI Grants 24107005 and 18033014. J.R. thanks Grant-in-Aid for JSPS Fellows. The crystallographic analyses were performed under the approval of the Photon Factory Program Advisory Committee (#2005G153 and #2010G092).

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- (27) In order to improve the reducing power of the Re-ring according to our previous report,²⁶ we introduced methyl groups into the bipyridine ligands. The redox potential for the first reduction of **R3e(5-dmb)³⁺** was -1.87 V vs Ag/AgNO₃ in DMF containing Et₄NBF₄ (0.1 M) as a supporting electrolyte (Figure S7c).
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- (29) In the case using [Re(5-dmb)(CO)₂(PPh₂Et)₂]⁺ (0.15 mM) instead of **R3e(5-dmb)³⁺** (0.05 mM) as a photosensitizer, Φ_{CO} was 60% and TON_{CO} was 563 (Figure S9).