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A Novel Tripodal Ligand, Tris[(4′-methyl-2,2′-bipyridyl-4-yl)methyl]carbinol and Its Trinuclear $\mathrm{Ru^{II}}$/$\mathrm{Re^{I}}$ Mixed-Metal Complexes: Synthesis, Emission Properties, and Photocatalytic CO_2 Reduction

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A novel tripodal ligand, tris[(4′-methyl-2,2′-bipyridyl-4-yl)methyl]carbinol (**L**), has been synthesized. The spectroscopic, electrochemical, and photocatalytic properties of the new trinuclear complexes (**Ru_2Re** and **$RuRe_2$**) linked by the tripodal bridging ligand **L** are then investigated. In addition, 2-fold-improved photocatalytic activities were obtained in the case of these trinuclear complexes compared to the mixtures of the appropriate monometallic model complexes in the reduction of CO_2 under visible irradiation.

Photophysical and photochemical properties of covalently linked polynuclear d^6 transition-metal complexes have been widely investigated in recent years.[1] Moreover, converting solar energy into chemical energy is one of the most important aspects relating to supramolecular complexes. For instance, these supramolecular complexes produce hydrogen and oxygen from water and reduce CO_2 by solar irradiation.[2] Such supramolecular complexes possess multiple functions: absorbing visible light, undergoing charge transfer, collecting electrons, and catalyzing the activation of small molecules.[3] In addition, a multielectron process is necessary for artificial photosynthesis.[4] As a matter of fact, a polynuclear complex could involve multicatalytic moieties to increase the photocatalytic properties and multiphotosensitizing sites, which could drive multielectron reactions after irradiation by visible light.[5] As reported previously, the dinuclear $\{\mathrm{Ru^{II}/Re^{I}}\}$ and tetranuclear $\{\mathrm{Ru^{II}/Re^{I}_3}\}$ complexes linked by an electronically inert bridge showed excellent photocatalytic properties for the reduction of CO_2 ($\mathrm{Ru^{II}} = [\mathrm{Ru(dmb)_3}]^{2+}$; $\mathrm{Re^{I}} = [\mathrm{(dmb)Re(CO)_3Cl}]$; dmb = 4,4′-dimethyl-2,2′-bipyridine).[6] Herein, we report on the synthesis and characterization of a new tripodal ligand L and its trinuclear heterometallic complexes containing $\mathrm{Ru^{II}}$ and $\mathrm{Re^{I}}$ moieties. Furthermore, the trinuclear complexes have been studied in the photocatalytic reduction of CO_2 to CO.

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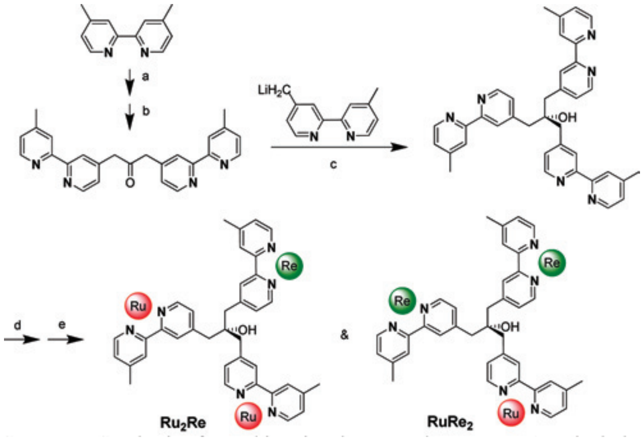
Scheme 1. Synthesis of **L** and Its Trinuclear Complexes[a]



[a] (a) LDA and ethyl formate; (b) Swern oxidation; (c) THF, −78 °C; (d) *cis*-[Ru(dmb)$_2$Cl$_2$], EtOH, reflux; (e) [Re(CO)$_5$Cl], EtOH, reflux.

The synthetic strategy of the novel tripodal ligand **L** is depicted in Scheme 1. **L** was synthesized by reacting 1,3-bis(4′-methyl-2,2′-bipyridyl-4-yl)propan-2-one with 4′-lithiated methyl-4-methyl-2,2′-bipyridine and then was isolated in 20% yield after purification by column chromatography (silica gel, chloroform, and ethyl acetate). Finally, **L** was satisfactorily characterized by NMR spectroscopy and elemental analyses, along with a mass peak at *m*/*z* 579 [M + 1].

The trinuclear heterometallic complexes **RuRe$_2$** and **Ru$_2$Re** were constructed by stepwise attachment of {Ru(dmb)$_2$}$^{2+}$ and then {Re(CO)$_3$Cl} units to the bipyridyl sites of **L**. First, the intermediate homometallic complexes [(dmb)$_2$Ru**L**]$^{2+}$ (**Y−Ru**) and [((dmb)$_2$Ru)$_2$**L**]$^{4+}$ (**Y−Ru$_2$**) were prepared by the reaction of the tripodal ligand **L** with an appropriate amount of Ru^{II} precursor, *cis*-[Ru(dmb)$_2$Cl$_2$]. The number of Ru^{II} units coordinated to **L** was controlled by a stoichiometric ratio of the starting materials, *cis*-[Ru(dmb)$_2$Cl$_2$] to **L**, in a reaction mixture. The heterometallic complexes were then prepared by introducing a stoichiometric amount of [Re(CO)$_5$Cl] to **Y−Ru** and **Y−Ru$_2$**, respectively. Finally, the complexes were purified on Sephadex LH-20 and then on silica gel [MeCN:H$_2$O:KNO$_3$ = 80:20:0.1 (M)] and subsequently converted to PF$_6^-$ salts by treatment with NH$_4$PF$_6$. In addition, the complexes generated in each synthetic step were fully characterized by electrospray ionization mass spectrometry, elemental analyses, and electronic and NMR spectroscopies.

The electronic absorption spectra of **RuRe$_2$** and **Ru$_2$Re** complexes in acetonitrile are identical with the superimposed spectra of the component units, respectively (see Figures 1 and S1 in the Supporting Information). In the trinuclear complexes, the individual component units were connected together via use of the tripodal bipyridyl ligand **L** as the bridging group. The bridging tripodal ligand did not affect the spectroscopic properties of the Ru^{II} and Re^{I} moieties in these trinuclear complexes. There were no significant interactions through the bridging linkage in the ground state. In addition, when both **Ru$_2$Re** and **RuRe$_2$** were excited at the rhenium(I) bipyridyl complex's metal-to-ligand charge-transfer (MLCT) absorption band (370 nm), only the strong MLCT emission from the excited Ru^{II} moieties was observed (see Figures 1 and S2 in the Supporting Information). This indicates that the Ru^{II} moieties are sensitized by the excited Re^{I} moieties through intramolecular energy-transfer processes in both **Ru$_2$Re** and **RuRe$_2$**. The absorption and emission spectroscopic data of the synthesized complexes are summarized in Table 1.

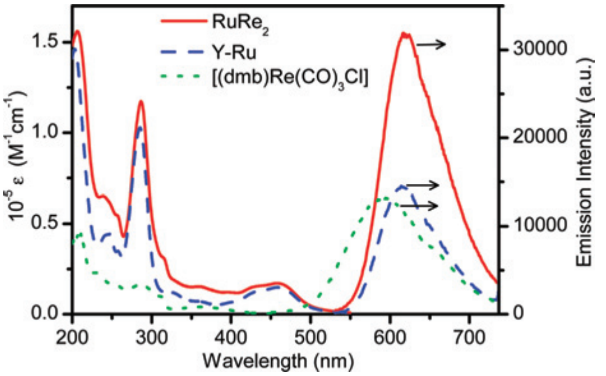


Figure 1. UV−vis and emission spectra of **RuRe$_2$** (red solid line), **Y−Ru** (blue dashed line), and [(dmb)Re(CO)$_3$Cl] (green dotted line). In the absorption measurement, all solutions are 10^{-5} M in acetonitrile at room temperature. In the emission measurement, **RuRe$_2$** (1×10^{-5} M), **Y−Ru** (1×10^{-5} M), and [(dmb)Re(CO)$_3$Cl] (2×10^{-5} M) are excited at 370 nm in acetonitrile.

Table 1. Absorption and Emission Spectroscopic Data

complex	λ_{max}, nm (ε, 10^4 M^{-1} cm^{-1})			λ_{em}, nm
[(dmb)Re(CO)$_3$Cl]	291 (1.60)	361 (0.40)		
Y−Ru	285 (10.3)		458 (1.50)	616
RuRe$_2$	286 (11.7)	361 (1.50)	458 (1.71)	621
Y−Ru$_2$	286 (15.7)		458 (2.79)	618
Ru$_2$Re	286 (17.4)	361 (1.80)	459 (3.06)	622

The oxidation and reduction potential data of the complexes were obtained by differential pulse voltammetry (DPV) using a glassy carbon working electrode in an acetonitrile solution with 0.1 M tetrabutylammonium perchlorate (see Table S1 in the Supporting Information). In the DPV oxidation window of **RuRe$_2$** and **Ru$_2$Re**, there are two well-resolved oxidation peaks that could be clearly assigned to the two kinds of metal centers, Ru^{II} and Re^{I}. For example, **RuRe$_2$** displayed Ru$^{II/III}$ and Re$^{I/II}$ oxidation at 1.25 and 1.10 V vs SCE, respectively. However, the first reduction waves of these complexes are unresolved broad ones in which both the bipyridyl parts of Ru^{II} and Re^{I} moieties are reduced almost simultaneously. Hence, there is no big energy gap between the one-electron-reduced Ru^{II} moiety and the reduced Re^{I} moiety.

In the case of **RuRe$_2$** and **Ru$_2$Re**, the intramolecular electron transfer from the reduced Ru^{II} moiety to the Re^{I} moiety could proceed smoothly ($\Delta G \approx -0.09$ eV). The results of the previous work[6] imply that the polynuclear complexes with weak coupling could be excellent photocatalysts. On the basis of these observations, **Ru$_2$Re** and **RuRe$_2$** were used as photocatalysts in the reduction of CO$_2$. The photocatalytic experiments were performed in a CO$_2$-saturated 5:1 dimethylformamide/triethanolamine (TEOA, as a proton capture agent) solution of the metal complexes with 1-benzyl-1,4-dihydronicotinamide (BNAH; 0.1 M) as a sacrificial donor under visible irradiation ($\lambda \geq 500$ nm) at

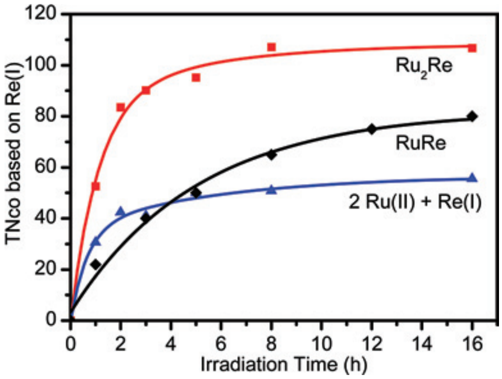


Figure 2. Turnover number of CO formation as a function of the irradiation time based on the Re^I moiety for **Ru$_2$Re**, a mixture of the monometallic model complexes, and a dinuclear {Ru^{II}−Re^I} complex with a bipodal ligand. For selective excitation of the Ru^{II} moiety, solutions were irradiated at $\lambda \geq 500$ nm using a high-pressure Hg lamp, in a merry-go-round irradiation apparatus, combined with a uranyl glass and a K_2CrO_4 (30% wt, optical length = 1 cm) solution filter. The concentration of the Re^I moiety was 0.025 mM, in a CO_2-saturated 5:1 DMF/TEOA (TEOA, as a proton capture agent) solution with BNAH (0.1 M) as a sacrificial donor.

room temperature. Furthermore, turnover numbers of CO formation (TN$_{CO}$, based on the complex concentration) for these trinuclear complexes were compared to that for the mixtures of the appropriate monometallic model complexes, namely, a stoichiometric mixture of $[Ru(dmb)_3]^{2+}$ and $[(dmb)Re(CO)_3Cl]$.

On the basis of the Ru^{II} moiety, **RuRe$_2$** (0.05 mM) exhibited 190 turnovers of CO formation compared to 89 for a mixture of the appropriate monometallic model complexes {$[Ru(dmb)_3]^{2+}$(0.05 mM) and $[(dmb)Re(CO)_3Cl]$ (0.1 mM)} after 16 h of irradiation. The photocatalytic activity of another trinuclear complex, **Ru$_2$Re**, was also examined under the same experimental conditions. For **Ru$_2$Re** (0.025 mM), 110 turnovers of CO formation were obtained based on the Re^I moiety, while for a mixture of the appropriate monometallic model complexes {$[Ru(dmb)_3]^{2+}$ (0.05 mM) and $[(dmb)Re(CO)_3Cl]$ (0.025 mM)}, 55 turnovers were generated (see Figure 2). These results indicate that the trinuclear complexes perform better as photocatalysts in the reduction of CO_2 than mixtures of the appropriate monometallic model complexes. Hence, the intramolecular electron transfer through the bridging tripodal ligand plays a crucial role in the photoinduced reduction of CO_2.

When TN$_{CO}$ was calculated based on the Ru^{II} moieties, the previously reported dinuclear {Ru^{II}−Re^I} and tetranuclear {Ru^{II}−Re$^I_3$} complexes with a bipodal bridging ligand [1,3-bis(4′-methyl-2,2′-bipyridine-4-yl)propan-2-ol][6] showed 160 and 240, respectively, compared to 190 for **RuRe$_2$**. These data suggest that the photocatalytic activities are enhanced with an increase of the molar ratio of Re^I to Ru^{II} in these polynuclear complexes.

In addition, when TN$_{CO}$ was considered based on the Re^I moiety, **Ru$_2$Re** showed 110 compared to 80 for the reported dinuclear {Ru^{II}−Re^I} with the bipodal bridging ligand.[6] The two photosensitizing moieties in one complex may thus be responsible for the more efficient electron transfer in the process of the photocatalytic CO_2 reduction.

In these trinuclear complexes, the Ru^{II} moieties were excited by visible irradiation and then quenched by a sacrificial reagent to form the one-electron-reduced species. A one-electron-reduced species of the Ru^{II} moiety could transfer one electron to a bipyridyl part of the Re^I moiety because the first reduction potentials of the Ru^{II} and Re^I moieties are almost the same. Therefore, the electron transfer takes place efficiently from the reduced Ru^{II} moieties to the Re^I moieties through the tripodal bridging ligand **L** ($\Delta G \approx -0.09$ eV) after visible irradiation. The mechanisms for the photocatalytic CO_2 reduction of **RuRe$_2$** and **Ru$_2$Re** are under investigation.

To summarize, enhancement of the photocatalytic response to visible light has been achieved by fabricating trinuclear complexes featuring covalently linked Ru^{II} and Re^I moieties using **L** as a bridging ligand. An artificial photocatalytic complex could be designed by providing multicatalytic and/or multiphotosensitizing units within a single molecule to enhance the function of the complex.

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Supporting Information Available: Experimental details and UV−vis absorption spectra (Figure S1), emission spectra (Figure S2) of **Ru$_2$Re**, and redox potential data (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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