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Architecture of Supramolecular Metal Complexes for Photocatalytic CO_2 Reduction: Ruthenium–Rhenium Bi- and Tetranuclear Complexes

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We study the electrochemical, spectroscopic, and photocatalytic properties of a series of Ru(II)–Re(I) binuclear complexes linked by bridging ligands 1,3-bis(4′-methyl-[2,2′]bipyridinyl-4-yl)propan-2-ol (bpyC_3bpy) and 4-methyl-4′-[1,10]phenanthroline-[5,6-*d*]imidazol-2-yl)bipyridine (mfibpy) and a tetranuclear complex in which three [Re(CO)$_3$Cl] moieties are coordinated to the central Ru using the bpyC_3bpy ligands. In the bpyC_3bpy binuclear complexes, 4,4′-dimethyl-2,2′-bipyridine (dmb) and 4,4′-bis(trifluoromethyl)-2,2′-bipyridine ({CF$_3$}$_2$bpy), as well as 2,2′-bipyridine (bpy), were used as peripheral ligands on the Ru moiety. Greatly improved photocatalytic activities were obtained only in the cases of [Ru{bpyC_3bpyRe(CO)$_3$Cl}$_3$]$^{2+}$ (**RuRe$_3$**) and the binuclear complex [(dmb)$_2$Ru(bpyC_3bpy)Re(CO)$_3$Cl]$^{2+}$ (**d$_2$Ru–Re**), while photocatalytic responses were extended further into the visible region. The excited state of ruthenium in all Ru–Re complexes was efficiently quenched by 1-benzyl-1,4-dihydronicotinamide (BNAH). Following reductive quenching in the case of **d$_2$Ru–Re**, generation of the one-electron-reduced (OER) species, for which the added electron resides on the Ru-bound bpy end of the bridging ligand bpyC_3bpy, was confirmed by transient absorption spectroscopy. The reduced Re moiety was produced via a relatively slow intramolecular electron transfer, from the reduced Ru-bound bpy to the Re site, occurring at an exchange rate ($\Delta G \sim 0$). Electron transfer need not be rapid, since the rate-determining process is reduction of CO_2 with the OER species of the Re site. Comparison of these results with those for other bimetallic systems gives us more general architectural pointers for constructing supramolecular photocatalysts for CO_2 reduction.

Introduction

Multinuclear metal complexes play a central role in the study of supramolecular structures as possible building blocks for photochemical and electrochemical molecular assemblies.[1] Many multinuclear compounds containing two or more metallic sites have been synthesized, and their optical, electronic, and photophysical properties have been studied.[1,2] In particular, ruthenium and rhenium polypyridine complexes are popular in both fundamental studies and applications.[3,4] These complexes form appealing subunits for nanoscaled

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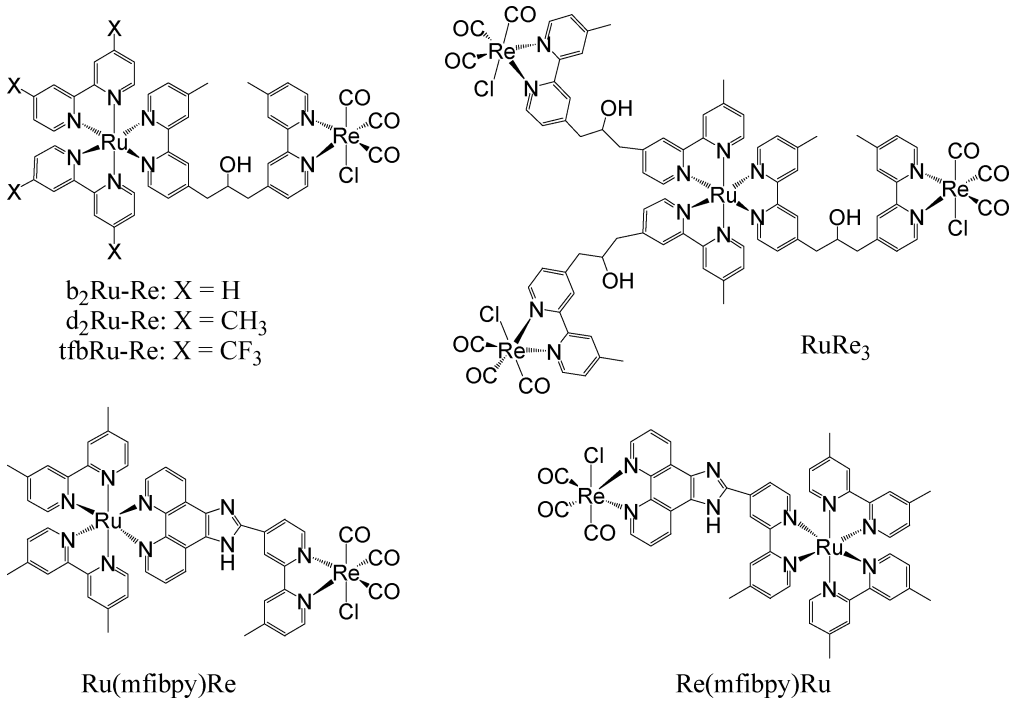

Figure 1. Schematic representation of the metal complexes and their abbreviations.

devices[5] because of their strong visible absorption, their advanced photochemical and redox properties, and their stability against photodecomposition.[6] There exist a number of means to fine-tune these features via made-to-order modifications on peripheral ligands.[7] Rhenium polypyridine complexes are known to act as photocatalysts and electrocatalysts for reducing CO_2 to CO.[8] A major problem with these photocatalysts is the lack of an extended absorption into the visible region. The present approach is to fabricate supramolecules of the rhenium complex linked covalently to the ruthenium complex as a visible-light absorber. We believe that this is the first report of the use of heteronuclear Ru and Re multimetallic complexes in the photocatalytic reduction of CO_2.[9]

Although some examples of mononuclear[10] and multinuclear[11] photocatalysts, such as Ru(II)−Co(III)[11a] and Ru(II)−Ni(II),[11d] have appeared in the literature, their activities for CO_2 reduction are not satisfactory. Although a mechanistic approach has been tried,[10] the controlling parameters that define structural requirements and electrochemical properties, which are essential in the design of new supramolecular photocatalysts, have not yet been systematically investigated. This study therefore aims also to learn how photocatalytic properties can be related to, and manipulated by, structural changes in such supramolecules. We are particularly interested in the assembly of multinuclear complexes involving different degrees of electronic communication between the metallic sites and "tunable" polypyridine ligands.

In this study, we describe the electrochemical, spectroscopic, and photocatalytic properties of a series of Ru(II)−Re(I) binuclear complexes linked by the bridging ligands (i) 1,3-bis(4′-methyl-[2,2′]bipyridinyl-4-yl)propan-2-ol ($bpyC_3$bpy)[12] and (ii) 4-methyl-4′-[1,10]phenanthroline-[5,6-*d*]imidazol-2-yl)bipyridine (mfibpy) and a tetranuclear complex **Ru(Re)$_3$** in which three [Re(CO)$_3$Cl] moieties are coordinated to the central Ru using the $bpyC_3$bpy ligands. Their structures are shown in Figure 1. In the case of the $bpyC_3$bpy complexes, a number of substituted bpy ligands, i.e., 4,4′-dimethyl-2,2′-bipyridine (dmb) and 4,4′-bis(trifluoromethyl)-2,2′-bipyridine ({CF_3}$_2$bpy), as well as 2,2′-bipyridine (bpy)

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itself, were used as peripheral ligands so as to fine-tune the electrochemical and photochemical properties of the supramolecular complexes.

Experimental Section

Instrumentation and Measurements. Absorption spectra were measured on a JASCO V-565 spectrophotometer. Emission spectra were recorded with a JASCO FP-6600 spectrofluorometer. These spectra were corrected for detector sensitivity using correction data supplied by JASCO on the FP-6600 system, and a single-mode Franck−Condon line-shape analysis was used to fit the emission spectra.[13a,b] The solutions were bubble degassed for 20 min with purified argon prior to measurements. Emission lifetimes of the metal complexes were measured with either a Horiba NAES-1100 time-correlated single-photon-counting system or a Continuum YG680-10 Nd^{3+}:YAG pulse laser source, as described previously.[13c] Nanosecond laser spectroscopy was employed to measure the transient absorption spectra and corresponding lifetimes.[13c]

Luminescence quenching experiments were made on argon-saturated solutions of at least five different concentrations of a sacrificial quencher. The values of k_q were calculated from linear Stern−Volmer plots for the luminescence of Ru ^{3}MLCT excited state and knowledge of its lifetime.

Electrospray ionization−mass spectroscopy (ESI-MS) was performed with a Shimadzu LCMS-2010A system, using HPLC-grade acetonitrile (MeCN) or CH_3OH/H_2O (1:1) as the mobile phase.

Redox potentials of metal complexes were measured by cyclic and differential-pulse voltammetry using an ALS/CHI CHI620 electrochemical analyzer in a standard three-cell electrode arrangement. Voltammograms were recorded using a platinum working electrode (diameter, 2 mm) in MeCN or a glassy-carbon (3 mm) in dimethylformamide (DMF) solutions of the complexes containing 0.1 M supporting electrolyte, tetra-*n*-butylammonium hexafluorophosphate (TBAH).

Photocatalytic reduction was performed in a 10-mL test tube (i.d. = 1 cm) containing 4 mL DMF/TEOA (5:1) solution of the metal complexes (0.05 mM) and a sacrificial reagent (0.1 M) after purging with CO_2 for 20 min. For a selective excitation of the ruthenium 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% w, $d = 1$ cm) solution filter. For the quantum yield measurements, an Ushio (Optical Modulex) Xe lamp SX-U1500H combined with a 480 nm (fwhm = 10 nm) band-pass filter, purchased from Asahi Spectra Co., and a 10-cm long $CuSO_4$ solution (250 g/L) filter were used. All experiments were conducted at the ambient temperature. Gas samples were taken using a gastight syringe. The gaseous reaction products, i.e., CO and H_2, were detected by GC-TCD. The incident light intensity was determined using a $K_3Fe(C_2O_4)_3$ actinometer. Formation of organic acids was checked by capillary electrophoresis system (CAPI-3300I Photal, Otsuka Electronics).

Materials. MeCN was purified by fractional distillation from P_2O_5 after having been dried for 1 day over 4 Å molecular sieves followed by distillation over CaH_2. DMF was dried over 4 Å molecular sieves and distilled at reduced pressure. Triethanolamine (TEOA) was also distilled at reduced pressure. All of the purified solvents were kept under Ar before use. The spectroscopic data were obtained on samples dissolved in the purified or spectral-grade solvents. Hydrated ruthenium trichloride was purchased from Kojima Chemical Co. and used as received. TBAH (Tokyo Kasei) was recrystallized from ethanol (EtOH). All other reagents were reagent-grade quality and were used without further purification.

Synthesis. 1-Benzyl-1,4-dihydronicotinamide (BNAH),[14] 1,10-phenanthroline-5,6-dione ($phenO_2$),[15] $[Ru(dmb)_2Cl_2]\cdot 2H_2O$,[16] and $[Ru(DMSO)_4Cl_2]$[17] were prepared according to the literature methods. 4-Methyl-2,2′-bipyridine-4′-carboxaldehyde (Mebpy-CHO),[18] 4,4′-bis(trifluoromethyl)-2,2′-bipyridine $(CF_3)_2bpy$, $[\{(CF_3)_2bpy\}_2RuCl_2]$,[19] and $[(bpy)_2Ru(bpyC_3bpy)Re(CO)_3Cl](PF_6)_2$, **$b_2$Ru−Re**,[12] were prepared as described previously. The synthesis and purification methods used for mfibpy and its mononuclear and binuclear complexes as well as the $Ru(Re)_3$ tetranuclear species are described below. All complexes were characterized by ^{1}H NMR, ESI-MS, FTIR, absorption, and emission spectroscopies.

(a) $[\{(CF_3)_2bpy\}_2Ru(bpyC_3bpy)](CF_3SO_3)_2$. To a solution of $bpyC_3bpy$ (900 mg, 2.27 mmol) in 50 mL of $MeOH/H_2O$ (9:1) was added $[\{(CF_3)_2bpy\}_2RuCl_2]$ (340 mg, 0.45 mmol) and $AgCF_3SO_3$ (250 mg, 0.97 mmol), and the argon-purged mixture was heated at reflux for 7 h under argon in dark condition. The reaction mixture was filtered over Celite while hot. The filtrate was concentrated to few milliliters and subjected to Sephadex LH20 chromatography, using MeOH as eluent. The product was precipitated from the concentrate by addition of water, filtered out and washed thoroughly with water, and vacuum-dried. Yield: 71%, 440 mg. Anal. Calcd for $C_{51}H_{36}F_{18}N_8O_7RuS_2$: C, 43.65; H, 2.77; N, 7.98. Found: C, 43.67; H, 2.80; N, 8.04. ESI-MS in MeCN (*m*/*z*): 541, $[M - 2CF_3SO_3]^{2+}$. ^{1}H NMR [CD_3CN] [δ in ppm (integration, multiplicity), assignment]: 2.51 (6H, s), methyl; 2.8−3.1 (4H, m), methylene; 3.18 (1H, br), OH; 4.26 (1H, br), methyne; 7.2−8.9 (24H, m), bpy ring protons.

(b) $[\{(CF_3)_2bpy\}_2Ru(bpyC_3bpy)Re(CO)_3Cl](PF_6)_2$, tfbRu−Re. The binuclear complex was prepared by reacting $[\{(CF_3)_2bpy\}_2Ru(bpyC_3bpy)](CF_3SO_3)_2$ (100 mg) and $Re(CO)_5Cl$ (30 mg) in 40 mL of MeOH for 35 h. After this period, the concentrate was subjected to Sephadex LH20 chromatography, using MeOH as eluent. The product was precipitated from the concentrate by addition of an aqueous solution of NH_4PF_6, filtered out and washed with water, and vacuum-dried. Yield: 91%, 110 mg. Anal. Calcd for $C_{52}H_{36}ClF_{24}N_8O_4P_2ReRu$: C, 37.23; H, 2.16; N, 6.68. Found: C, 37.21; H, 2.42; N, 6.46. ESI-MS in MeCN (*m*/*z*): 694, $[M - 2PF_6]^{2+}$; 1533, $[M - PF_6]^+$.

(c) $[(dmb)_2Ru(bpyC_3bpy)Re(CO)_3Cl](PF_6)_2$, d_2Ru−Re. The binuclear complex was prepared by the method described for $[(bpy)_2Ru(bpyC_3bpy)Re(CO)_3Cl](PF_6)_2$.[12] Briefly, $[(dmb)_2Ru(bpyC_3bpy)]Cl_2$ (70 mg) and $Re(CO)_5Cl$ (28 mg) were reacted in 100 mL of 1,2-dichloroethane for 3 h. After this period, the product was precipitated from the concentrate by addition of NH_4PF_6(aq), filtered out, and washed with water. The crude was subjected to column chromatography on SP Sephadex C-25 using a 1:1 mixture of MeCN and aqueous buffer (pH 5.0, containing 20 mM NH_4PF_6) as eluant, followed by precipitation of the product from the concentrate and filtration. The product was dissolved in 50 mL of

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acetone/H_2O (1:1) containing 0.1 M NH_4Cl and heated at reflux condition for 30 min. The product was reprecipitated from the concentrate by addition of an aqueous solution of NH_4PF_6, filtered out and washed with water, and vacuum-dried. Yield: 90%, 95 mg. Anal. Calcd for $C_{52}H_{48}ClF_{12}N_8O_4P_2ReRu$: C, 42.73; H, 3.31; N, 7.67. Found: C, 42.45; H, 3.61; N, 7.41. ESI-MS in MeCN (*m*/*z*): 586, $[M - 2PF_6]^{2+}$; 1317, $[M - PF_6]^+$.

(d) 4-Methyl-4′-[1,10]phenanthroline-[5,6-*d*]imidazol-2-yl)-bipyridine, mfibpy. A portion of 96 mg (0.46 mmol) of $phenO_2$ in hot EtOH (25 mL) was added to a mixture of 90 mg (0.46 mmol) of MebpyCHO and 0.5 g of ammonium acetate in 25 mL of EtOH. The mixture was allowed to reflux for 3 h and then cooled. The volume of the reaction was reduced to ca. 5 mL by rotary evaporation. After addition of water to the concentrate, a yellow precipitate was formed. The crude product was filtered out and washed with water. It was recrystallized from a mixture of EtOH and water. Yield: 51%, 90 mg. Anal. Calcd for $C_{24}H_{16}N_6$: C, 74.21; H, 4.15; N, 21.64. Found: C, 74.48; H, 4.08; N, 21.42.

(e) [(MebpyCHO)Re(CO)$_3$Cl]. A mixture of $[Re(CO)_5Cl]$ (150 mg, 0.41 mmol) and MebpyCHO (82 mg, 0.41 mmol) in 100 mL of argon-purged toluene was refluxed for 3 h. The reaction mixture turned red within few minutes, and an orange-red precipitate was gradually formed. It was then cooled, and the orange precipitate was filtered off, washed with toluene and hexane, and vacuum-dried. Yield: 95%, 198 mg. Anal. Calcd for $C_{15}H_{10}ClN_2O_4Re$: C, 35.75; H, 2.00; N, 5.56. Found: C, 35.99; H, 1.98; N, 5.44. ^{1}H NMR (CD_3CN) [δ in ppm (integration, multiplicity), assignment]: 10.17 (1H, s), CHO; 9.26 (1H, d), 6′; 8.86 (1H, d), 6; 8.78 (1H, s), 3′; 8.44 (1H, s), 3; 7.97 (1H, dd), 5′; 7.51 (1H, dd), 5; 2.59 (3H, s), methyl.

(f) [(mfibpy)Re(CO)$_3$Cl]. To a mixture of 60 mg (0.12 mmol) of $[(MebpyCHO)Re(CO)_3Cl]$ and 0.5 g of ammonium acetate in 25 mL of EtOH was added 40 mg (0.19 mmol) of $phenO_2$ dissolved in hot EtOH (25 mL). The mixture was allowed to reflux for 3 h and then was cooled. The volume of the reaction was reduced to ca. 5 mL by rotary evaporation. After addition of water to the concentrate, a brown precipitate was formed. The crude product was filtered out and washed with water. It was recrystallized from acetone and vacuum-dried. Yield: 93%, 77 mg. Anal. Calcd for $C_{27}H_{16}ClN_6O_3Re{\cdot}CH_3COCH_3$: C, 47.90; H, 2.95; N, 11.17. Found: C, 47.93; H, 2.84; N, 10.82. ESI-MS in MeCN (*m*/*z*): 700.9, $[M - Cl + MeCN]^+$. ^{1}H NMR (CD_3CN) [δ in ppm (integration, multiplicity), assignment]: 9.27 (1H, d), c′; 9.23 (1H, dd), a′; 9.21 (1H, dd), 6′; 9.13 (1H, s), 3′; 8.93 (1H, d), c; 8.89 (1H, dd) a; 8.78 (1H, dd), 6; 8.57 (1H, s), 3; 8.10 (2H, m), 4′; 7.98 (2H, m), 4; 7.86 (1H, dd), b′; 7.78 (1H, dd), b; 7.83 (2H, dd), 6′; 8.35 (1H, dd), b′; 7.94 (1H, dd), 5′; 7.90 (1H, dd), b; 7.51 (1H, dd), 5; 2.64 (3H, s), methyl.

(g) [(dmb)$_2$Ru(mfibpy)Re(CO)$_3$Cl](PF$_6$)$_2$, Ru(mfibpy)Re. $[(mfibpy)Re(CO)_3Cl]$ (35 mg) and $[Ru(dmb)_2Cl_2]{\cdot}2H_2O$ (28 mg) were allowed to react in argon-purged ethylene glycol (5 mL) at 150 °C. After 1 h, the reaction mixture was cooled to room temperature, and the product was precipitated by addition of an aqueous solution of NH_4PF_6 (15 mL). The orange precipitate was filtered off, washed with water, and recrystallized by slow evaporation of acetone from an aqueous solution. The product can further be purified by column chromatography on SP Sephadex C-25 using a 1:1 mixture of MeCN and aqueous buffer (pH 5.0, containing 20 mM NH_4PF_6) as eluant, followed by precipitation of the product from the concentrate by adding NH_4PF_6(aq) and recrystallization in EtOH/H_2O. Yield: 36%, 26 mg. Anal. Calcd for $C_{51}H_{40}F_{12}ClN_{10}O_3P_2ReRu$: C, 42.14; H, 2.77; N, 9.64. Found: C, 42.44; H, 3.04; N, 9.86. ESI-MS in MeCN (sample dissolved in acetone) (*m*/*z*): 582, $[M - 2PF_6]^{2+}$; 612, $[M - 2PF_6 + CH_3COCH_3]^{2+}$.

(h) [(dmb)$_2$Ru(MebpyCHO)](PF$_6$)$_2$. A mixture of $[Ru(dmb)_2Cl_2]{\cdot}2H_2O$ (68 mg, 0.12 mmol) and MebpyCHO (30 mg, 0.15 mmol) in 50 mL of EtOH/H_2O (4:1) was refluxed for 7 h. The solution was then cooled to room temperature and concentrated. A saturated solution of NH_4PF_6 in water was added to the concentrate. The orange precipitate was filtered off and washed with cold water. The product was subjected to column chromatography on SP Sephadex C-25 using a 1:1 mixture of MeCN and aqueous buffer (pH 5.0) as eluant. A center cut of the orange band was collected. A saturated solution of NH_4PF_6 in H_2O was again added to the concentrate, and the precipitate was recrystallized from MeOH/H_2O. Yield: 62%, 70 mg. Anal. Calcd for $C_{36}H_{34}F_{12}N_6OP_2Ru$: C, 45.15; H, 3.58; N, 8.78. Found: C, 45.12; H, 3.84; N, 8.48. ESI-MS in MeCN (*m*/*z*): 334, $[M - 2PF_6]^{2+}$; 813, $[M - PF_6]^+$.

(i) [(mfibpy)Ru(dmb)$_2$](PF$_6$)$_2$, (mfibpy)Ru. A mixture of $[Ru(dmb)_2Cl_2]{\cdot}2H_2O$ (40 mg, 0.07 mmol) and mfibpy (40 mg, 0.07 mmol) in 50 mL of EtOH/H_2O (4:1) was refluxed for 4 h. The reaction mixture was cooled and concentrated by rotary evaporation. A saturated solution of NH_4PF_6 in water was added to the concentrate, and the orange precipitate that formed was filtered off and washed with water. The product was subjected to column chromatography on SP Sephadex C-25 using a 1:1 mixture of MeCN and aqueous buffer (pH 5.0) as eluant. A center cut of the first orange band was collected. The second orange-red band is the binuclear complex, $[(dmb)_2Ru(mfibpy)Ru(dmb)_2](PF_6)_4$, and can be eluted by increasing concentration of NH_4PF_6 in the buffer. A saturated solution of NH_4PF_6 in H_2O was again added to the concentrate, and the precipitate was recrystallized from MeOH/H_2O. Yield: 54%, 43 mg. Anal. Calcd for $C_{48}H_{40}F_{12}N_{10}P_2Ru$: C, 50.22; H, 3.51; N, 12.20. Found: C, 49.95; H, 3.77; N, 11.91. ESI-MS in MeCN (*m*/*z*): 429, $[M - 2PF_6]^{2+}$; 857, $[M - 2PF_6 - H]^+$; 1003, $[M - PF_6]^+$. ^{1}H NMR (acetone-d_6) [δ in ppm (integration, multiplicity), assignment]: 9.19 (1H, s), 3‴; 8.92 (2H, d), aa′; 8.66 (1H, d), 6‴; 8.62 (1H, d), c′; 8.40 (2H, s), 3′; 8.37 (2+1H, s), 3 and c; 8.32 (1H, s), 3″; 8.01 (2H, dd), bb′; 7.66 (3H, d), 6′ and 6″; 7.57 (1H, d), 5‴; 7.46 (2H, d), 6; 7.30 (2H, d), 5′; 7.25 (1H, d), 5″; 7.09 (2H, d), 5; 2.58 (6H, s), 2.56 (3H, s) and 2.48 (6H, s), methyls.

(j) [Cl(CO)$_3$Re(mfibpy)Ru(dmb)$_2$](PF$_6$)$_2$, Re(mfibpy)Ru. $[(mfibpy)Ru(dmb)_2](PF_6)_2$ (25 mg) and $[Re(CO)_3Cl]$ (8 mg) were allowed to react in argon-purged ethylene glycol (3 mL) at 160 °C. After 10 min, the reaction mixture was cooled to room temperature, and the product was precipitated by addition of an aqueous solution of NH_4PF_6 (15 mL). The brown precipitate was filtered off and washed with water. The crude was purified by column chromatography on SP Sephadex C-25 using a 1:1 mixture of MeCN and aqueous buffer (pH 5.0, containing 10 mM NH_4PF_6) as eluant, followed by precipitation of the product from the concentrate by adding NH_4PF_6(aq). The recrystallization performed in MeCN/MeOH/NH_4PF_6(aq). Yield: 50%, 15.4 mg. Anal. Calcd for $C_{51}H_{40}F_{12}ClN_{10}O_3P_2ReRu$: C, 42.14; H, 2.77; N, 9.64. Found: C, 42.08; H, 2.99; N, 9.47. ESI-MS in MeCN (*m*/*z*): 582, $[M - 2PF_6]^{2+}$.

(k) [Ru{bpyC$_3$bpyRe(CO)$_3$Cl}$_3$](PF$_6$)$_2$, RuRe$_3$. $Ru(DMSO)_4Cl_2$ (407 mg) and $bpyC_3bpy$ (1 g) were allowed to react in EtOH/H_2O (50:1) at reflux condition for 48 h. Then the solvent was evaporated and the residue was subjected to column chromatography on Sephadex LH-20 using EtOH as solvent which gave analytically pure $Ru(bpyC_3bpy)_3Cl_2$ (yield 59%, 680 mg). The resulted complex $Ru(bpyC_3bpy)_3Cl_2$ (50 mg) and $Re(CO)_5Cl$ (46 mg) were allowed to react in argon-purged EtOH/DMF (50:10) at reflux. After 24 h,

Table 1. Turnover Number (TN_{CO}), CO Production Yields (Φ_{CO}), and Quenching Rate (k_q) and Fractions (η_q)

compd	TN_{CO}[a]	Φ_{CO}[b]	$10^{-8}k_q$[c]/M^{-1} s^{-1}	η_q[d]
mixed Ru and Re (1:1)[e]	101	0.062	0.26	0.71
d_2Ru−Re	170	0.120	1.4	0.90
b_2Ru−Re	50[f]		2.3	0.95
tfbRu−Re	3		61	∼1.0
Ru(mfibpy)Re	14		0.75	0.8
Re(mfibpy)Ru	28[g]		1.5	0.95
$RuRe_3$	240	0.093	2.8	0.96

[a] TN_{CO} is the turnover number for production of CO following 16 h of irradiation; [complex] = 0.05 mM. [b] The best value obtained following 40 min irradiation at 480 nm ($I = 1.54 \times 10^{-6}$ einstein/min) in CO_2-saturated solutions. [c] The values were obtained at room temperature and in N_2-saturated DMF/TEOA (5:1) solutions containing metal complexes and BNAH as the sacrificial reagent. In the calculation of k_q, the excited-state lifetimes measured in MeCN were applied. [d] Quenching fractions of ^{3}MLCT by 0.1 M BNAH. [e] Mixed solution of $[Ru(dmb)_3]^{2+}$ and $[(dmb)Re(CO)_3Cl]$. [f] After 12.5 h. [g] After 18.5 h.

the solvent was evaporated to dryness and the residue was subjected to column chromatography on Sephadex LH-20 using MeOH/MeCN (7:3) as eluent. Only a center cut of the main band was collected, and the product was obtained from the concentrate upon standing. The recrystallization performed in MeCN/EtOH. Yield: 50%, 41.7 mg. Anal. Calcd for $C_{84}H_{72}Cl_5N_{12}O_{12}Re_3Ru$: C, 44.28; H, 3.19; N, 7.38. Found: C, 43.99; H, 3.44; N, 7.10. ESI-MS in MeCN (*m*/*z*): 738, $[M - 2PF_6 - Cl + MeCN]^{3+}$; 1104, $[M - 2PF_6]^{2+}$. ^{1}H NMR (DMSO-d_6) [δ in ppm (integration, multiplicity), assignment]: 8.87 and 8.83 (12H, d), 6 and 6′; 8.68 and 8.64 (12H, s), 4 and 4′; 7.61 and 7.57 (12H, d), 5 and 5′; 5.21 (3H, br), CH; 4.31 (12H, br), CH_2; 3.30 (18H, s), CH_3.

Results

Photocatalytic Reduction of CO_2. Good photocatalytic activities were obtained when the tetranuclear complex **$RuRe_3$** or the binuclear complex **d_2Ru−Re** was used in the reduction of CO_2 (Table 1). In both cases, carbon monoxide (formed catalytically) and a very small amount of dihydrogen were produced. No formic acid was observed in the reaction solution after the irradiation. The quantum yields of CO formation were 0.120 and 0.093 for **d_2Ru−Re** and **$RuRe_3$** respectively, using 480-nm monochromatic light at 1.54×10^{-6} einstein/min. Figure 2 shows the turnover numbers (TN_{CO}, mol of the CO produced/mol of the complex) versus the irradiation time. The bi- and tetranuclear photocatalysts respectively exhibited turnover numbers of 170 and 240 for CO formation after 16 h of light irradiation. A 1 mL reaction solution with **d_2Ru−Re** was added, after 7-h irradiation, to 10 mL of 1:1 solution of acetonitrile mixed with aqueous buffer (pH 1.8), and this solution was then subjected to column chromatography on SP-Sepahdex C-25 using a 1:1 mixture of acetonitrile and aqueous buffer (pH 5.0, containing 20 mM NH_4PF_6). The main band was collected, and acetonitrile was evaporated. The precipitate was washed with water and analyzed by the ESI-MS spectrometer, with acetonitrile as eluent. Peaks attibutable to the Cl^--substituted complex $[(bpy)_2Ru(bpyC_3bpy)Re(CO)_3(MeCN)]^{3+}$, with which the acetonitrile ligand should coordinate during the post-treatments, were observed at $m/z = 393$, $[M]^{3+}$, and 661, $[M + PF_6^-]^{2+}$, with peaks attributed to the starting complex

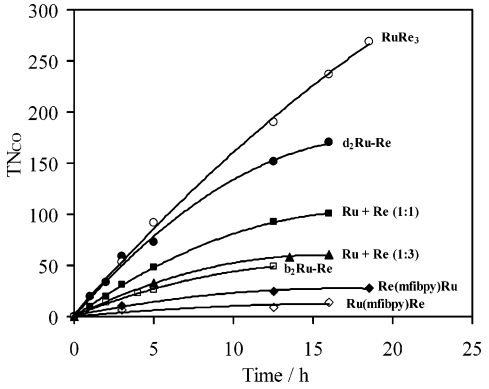


Figure 2. Turnover number for production of CO from CO_2 as a function of irradiation time. For selective excitation of the ruthenium moiety, solutions were irradiated at $\lambda \geq 500$ nm using a high-pressure Hg lamp, in a merry-go-round irradiation apparatus, combined with a uranyl glass and a K_2CrO_4 (30% w, $d = 1$ cm) solution filter. The concentration of the photocatalysts used is 0.05 mM, in a CO_2-saturated DMF/TEOA (5:1) solution containing 0.1 M of the sacrificial reagent BNAH.

d_2Ru−Re. Catalytic formation of CO continued after 7-h irradiation, as shown in Figure 2.

An equimolar mixed solution of $[Ru(dmb)_3]^{2+}$ and $[(dmb)Re(CO)_3Cl]$, which is a model of **d_2Ru−Re**, had a turnover number of 100 after 16-h irradiation, when it reached its plateau. In mixed solutions of the mononuclear complexes, an increase in the concentration of $[(dmb)Re(CO)_3Cl]$ caused a decrease in TN_{CO}. For example, after 16-h irradiation of a solution containing 0.05 mM of $[Ru(dmb)_3]^{2+}$ and 0.15 mM of $[(dmb)Re(CO)_3Cl]$, a model of **$RuRe_3$**, TN_{CO} was only 61 on the basis of the $[Ru(dmb)_3]^{2+}$ used (Figure 2). In the absence of $[Ru(dmb)_3]^{2+}$, a mononuclear Re complex $[(dmb)Re(CO)_3Cl]$ gave a turnover number of only ca. 15 under the same conditions except that 365-nm excitation was used. Without addition of the rhenium complex, $[Ru(dmb)_3]^{2+}$ did not itself show any photocatalytic activity for CO_2 reduction.

The photocatalytic abilities of the binuclear complexes with the mfibpy bridging ligand, i.e., **Ru(mfibpy)Re** and **Re(mfibpy)Re**, were much inferior to those with the $bpyC_3$-bpy ones **d_2Ru−Re** and **$RuRe_3$**. In the case where $(CF_3)_2$-bpy or bpy were used as peripheral ligands, the binuclear complexes also had poor photocatalytic ability, i.e., showing TN_{CO} of 3 and 50 respectively using **tfbRu−Re** and **b_2Ru−Re** (Figure 2).

Absorption and Emission Properties. Absorption and emission maxima, molar extinction coefficients, and emission lifetimes for the complexes are summarized in Table 2. Absorption and emission spectra of typical examples are shown in Figures 3 and 4. Absorption features appearing in the visible region at 365 and 400−550 nm correspond to spin-allowed ^{1}MLCT transitions initiated from the Re and Ru centers, respectively. The intense absorption band in the UV region (ca. 287 nm) is due to ligand-centered ($\pi-\pi^*$) transitions associated mainly with the polypyridine units.

In the $bpyC_3bpy$ complexes, the spectra exhibited by the binuclear complexes match with a sum spectrum of the model complexes for each component unit, for example $[Ru(dmb)_3]^{2+}$ and $[(dmb)Re(CO)_3Cl]$. As shown in Figure 3A, in the case of **d_2Ru−Re**, there was no detectable perturbation

Table 2. Spectroscopic and Photophysical Properties of the Ru and Re Complexes[a]

complex	λ_{abs}[b]/nm ($10^{-3}\epsilon_{max}$[c]/M^{-1} cm^{-1})		λ_{em}[b]/nm (298 K)	E_{00}[d]/cm^{-1} (298 K)	τ[e]/ns (298 K)
	$\pi-\pi^*$	MLCT			
d_2Ru−Re	287 (94.5)	459 (14.9)	631	15 920	750
b_2Ru−Re	239 (42.3), 288 (89.7)	453 (14.1)	631	15 840	800
tfbRu−Re	242 (42.6), 296 (77.9)	478 (11.6)	671	14 870	560
Ru(mfibpy)Re	248 (58.8), 282 (103)	442 (24.2)	646	15 530	930
$[(mfibpy)Ru(dmb)_2]^{2+}$	248 (47.8), 285 (96.9)	466 (18.2)	638	15 730	1520
Re(mfibpy)Ru	248 (45.3), 286 (85.6)	457 (26.0)	637	15 780	1390
$RuRe_3$	291 (95.4)[f]	462 (12.7)[e]	638[e]	15 920[e]	860

[a] The values were obtained in MeCN at room temperature unless otherwise noted. [b] Uncertainties in λ_{abs} and λ_{em} are ±1 nm. [c] Estimated error in ϵ_{max} is ±5%. [d] Estimated error in E_{00} is ±30 cm^{-1}. [e] Uncertainty in lifetime values is <6%. [f] In DMF at room temperature.

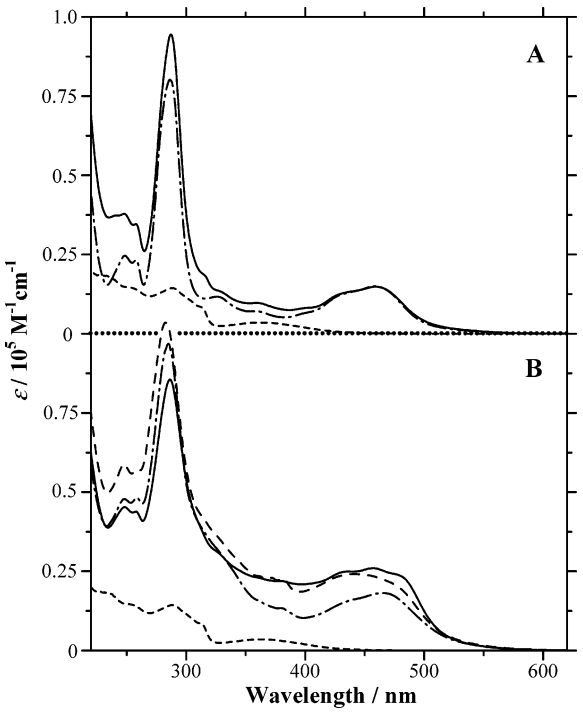


Figure 3. Room-temperature absorption spectra of metal complexes in MeCN: (A) [(dmb)Re(CO)$_3$Cl] (dashed line), [(dmb)$_2$Ru(bpyC$_3$bpy)](PF$_6$)$_2$ (dotted−dashed line), **d$_2$Ru−Re** (solid line); (B) [(dmb)$_2$Ru(mfibpy)](PF$_6$)$_2$ (dotted−dashed line), **Ru(mfibpy)Re** (dashed line), **Re(mfibpy)Ru** (solid line).

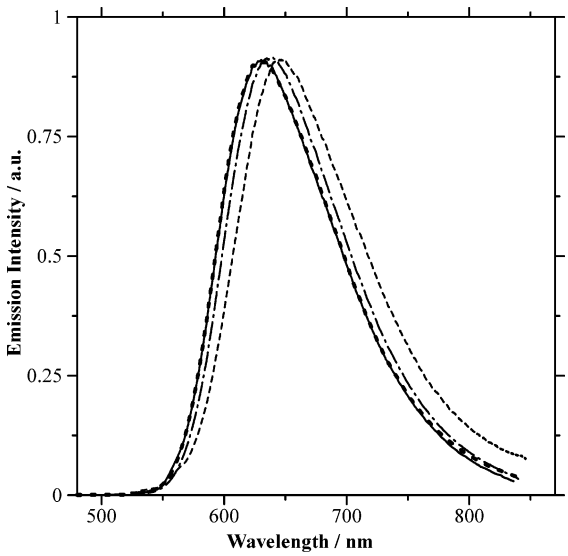


Figure 4. Corrected emission spectra of **Ru(mfibpy)Re** (dashed line), [(mfibpy)Ru(dmb)$_2$](PF$_6$)$_2$ (dotted−dashed line), and [(dmb)$_2$Ru(bpyC$_3$bpy)](PF$_6$)$_2$ (solid line) at room temperature in MeCN solution. For comparison, the spectrum of [Ru(dmb)$_3$](PF$_6$)$_2$ (dotted line) is also superimposed on the solid line (λ_{ex} = 460 nm).

in these spectra, indicating that the electronic communication across the bridge is very weak. For **tfbRu−Re**, the MLCT absorption peaked at a longer wavelength (Table 2), showing clearly that as a result of the strong σ-withdrawing character of CF_3 substituents, the ligand π^* orbitals are stabilized and the lowest lying MLCT state is localized on the peripheral ligands, i.e., $(CF_3)_2$bpy. As for **b$_2$Ru−Re**, the lowest MLCT absorption could be assigned to either the bridge or peripheral ligands in view of the broad nature of the MLCT band.

In the mfibpy complexes, weak bands in the 360−380-nm range may also be assigned to the bridging ligand. In the binuclear complexes, the ^{1}MLCT absorption of the Re center seems to be obscured by these bands. The MLCT band shapes due to the Ru center were in all the mfibpy binuclear complexes different from that in the Ru mononuclear complex $[(mfibpy)Ru(dmb)_2]^{2+}$ (Figure 3B). The bridging ligand mfibpy is a fully π-conjugated system mediating strong electronic communication between the metal centers. Therefore, in the binuclear complexes, new molecular orbital coefficients contribute in constructing the MLCT absorption band.

The luminescence of the binuclear complexes with bpyC$_3$-bpy can be described using an energy diagram on the basis of superimposing the lowest excited states of the Ru and Re moieties. An efficient quenching of emission at wavelengths shorter than 600 nm, which comes predominantly from the Re moiety, and enhancement of emission intensity at wavelengths longer than 600 nm, which is from the Ru moiety, were observed. It follows that the emission spectra of the binuclear complex **d$_2$Ru−Re** are identical with the corresponding Ru mononuclear $[(dmb)_2Ru(bpyC_3bpy)]^{2+}$, as depicted in Figure 4. We therefore conclude that an intercomponent energy transfer occurs from an upper lying Re excited state of the [(bpyC$_3$bpy)Re(CO)$_3$Cl] moiety to the lower lying Ru ^{3}MLCT excited state of the [(dmb)$_2$Ru(bpyC$_3$-bpy)] subunit in these supramolecular complexes. In the cases of **tfbRu−Re** and **b$_2$Ru−Re**, similar energy transfer from the Re moiety to the Ru was observed. A detailed study of the energy transfer mechanism and rates for **b$_2$Ru−Re** has been addressed previously.[12]

In the binuclear complexes with mfibpy, efficient quenching of the Re excited state was also observed. However, as

Table 3. Redox Potentials of Ru and Re Complexes (V)[a]

compd	$E_{1/2}$(oxdn)	$E_{1/2}$(redn)	$E_{1/2}$* (redn)
$[Ru(dmb)_3]^{2+}$ [b]	+0.74	−1.77, −1.96, −2.22	+0.20
$[(dmb)_2Ru(bpyC_3bpy)]^{2+}$	+0.77	−1.76, −1.95, −2.22, −2.55	
$[(dmb)Re(CO)_3Cl]$	+0.92	−1.78, −1.98, −2.15, −2.3	
$[(mfibpy)Re(CO)_3Cl]$	+0.90	−1.41,[c] −1.80, −2.28, −2.54	
$[(mfibpy)Ru(dmb)_2]^{2+}$	+0.81	−1.28, −1.50, −1.82, −2.03	+0.67
d_2Ru-Re	+0.75, +0.94	−1.77,[c] −1.97, −2.24	+0.20
b_2Ru-Re	+0.85, +1.13	−1.73, −1.87, −1.96, −2.01	+0.23
tfbRu−Re	+0.94, +1.14	−1.23, −1.41, −1.76, −1.87	+0.61
Ru(mfibpy)Re	+0.89, +1.04	−1.10, −1.33, −1.65, −1.80	+0.83
Re(mfibpy)Ru	+0.81, +1.01	−1.10, −1.28, −1.50, −1.63	+0.86
$RuRe_3$ [b]	+0.77, +0.91	−1.80,[d] −2.04, −2.34	+0.17

[a] The values were obtained at room temperature and in MeCN solutions containing 0.1 M TBAH. All $E_{1/2}$ values are referenced to the $E_{1/2}$ of the $Ag/AgNO_3$ redox couple (0.32 V vs SCE in MeCN); for comparison, the redox potentials of $[Ru(dmb)_3]^{2+}$ are also presented. [b] In DMF (0.1 M TBAH). [c] Two-electron reduction. [d] Broad but very close to a three-electron reduction.

a result of strong electronic communication between the metal centers in the **Ru(mfibpy)Re** complex, we found that the luminescence band maximum was at lower energy (646 nm) for the binuclear complexes than for the mononuclear complex (Figure 4). This behavior is due to a stabilizing effect, as a result of coordination to the second metal center, on the π^* level of the imidazolyl motif of the bridging ligand mfibpy that is involved in the MLCT excited-state responsible for the luminescence.

We conclude that the lowest lying luminescent level is Ru-centered in all of the supramolecular complexes. Also, since we performed a selective excitation of the Ru-based chromophore at $\lambda_{ex} = 480$ nm in quantum yield measurements, or $\lambda_{ex} \geq 500$ nm in photocatalytic reduction of CO_2, we consider only reductive quenching of the Ru ^{3}MLCT excited state in the following sections.

Electrochemical Properties. The electrochemical behavior of the complexes is summarized in Table 3. The redox processes of the individual components were maintained in all of the $bpyC_3bpy$ complexes. The cyclic voltammograms of the complexes were consistent with metal-based oxidation and several ligand-based reductions. We can assign the first reduction wave to the peripheral ligands in **tfbRu−Re** (at −1.23 V vs Ag/Ag^+ in MeCN containing 0.1 M TBAH) by analogy with $[((CF_3)_2bpy)_2Ru(dmb)]^{2+}$ (−1.21 V). In the case of **d_2Ru−Re**, the first reduction wave at −1.77 V corresponds to a two-electron reduction. At this potential the Ru and Re sites of the $bpyC_3bpy$ bridging ligand should both be reduced, since the first reduction wave in the model complexes $[Ru(dmb)_3]^{2+}$ and $[(dmb)Re(CO)_3Cl]$ were observed at −1.77 and −1.78 V, respectively. This implies that there is no strong electronic interaction between either end of the bridging ligand in the OER species of **d_2Ru−Re**. In the case of **b_2Ru−Re**, the first two reduction waves (at ca. −1.73 and −1.87 V) are poorly resolved so that assignment is rather difficult. Since the first reduction in the model complexes $[(bpy)_2Ru(dmb)]^{2+}$ and $[(dmb)Re(CO)_3Cl]$ happens at −1.68 and −1.78 V, respectively, these could be assigned to sequential reductions of the bpy ligand of the ruthenium site and the bridging ligand on the rhenium end.

In line with these results and on the basis of the known correlation between electrochemical and spectroscopic properties,[3,6,20] the lowest lying MLCT state in **tfbRu−Re** is expected to reside on the peripheral $(CF_3)_2bpy$ ligand, due to the strong σ-withdrawing character of the CF_3 substituents.[19] This is responsible for a shift of 0.40 V in the first reduction potential of **tfbRu−Re** compared to **b_2Ru−Re**. In the case of **d_2Ru−Re**, a bridging ligand localization of the lowest lying MLCT state is expected.

By comparing the first reduction potentials observed for mononuclear complexes with mfibpy ligand $[(mfibpy)Re(CO)_3Cl]$ and $[(dmb)_2Ru(mfibpy)]^{2+}$ at −1.44 and −1.29 V, respectively, with those of corresponding reference complexes of $[(dmb)Re(CO)_3Cl]$ and $[Ru(dmb)_3]^{2+}$, we can assign the first reduction wave to the bridging ligand mfibpy. Introduction of the second metal into the complex shifted the potentials anodically to ca. −1.10 V in both the **Ru(mfibpy)Re** and **Re(mfibpy)Ru** binuclear complexes. This is due to stabilization of the π^* LUMO localized on the mfibpy. The inequivalence of the binding sites in mfibpy is indicated by comparing the metal oxidation potentials in two binuclear complexes as well as their respective mononuclear complexes $[(mfibpy)Re(CO)_3Cl]$ and $[(mfibpy)Ru(dmb)_2]^{2+}$. For **Ru(mfibpy)Re**, the first oxidation wave occurred at a potential more positive (+0.89 V) than those of the $Ru^{3+/2+}$ couple in **Re(mfibpy)Ru** and $[(mfibpy)Ru(dmb)_2]^{2+}$ (both at +0.81 V). This clearly shows that the Ru in **Ru(mfibpy)-Re** is coordinated to the phenanthroline site of the mfibpy, which has a higher π acceptability than the other bpy site.[6] In $[(mfibpy)Re(CO)_3Cl]$, the $Re^{2+/+}$ wave is at a potential similar to that in $[(dmb)Re(CO)_3Cl]$. However, in **Ru(mfibpy)Re** and **Re(mfibpy)Ru**, the Re oxidation wave was shifted positively by up to 140 mV due to electrostatic interaction between the metal centers. It is apparent that the mfibpy ligand allows substantial electronic communication across the bridge.

Discussion

We have successfully synthesized a number of bi- and tetranuclear supramolecular complexes in the development of CO_2 reduction photocatalysts. These are constructed with an photosensitizer part, using the ruthenium(II) bpy-type complex, and a catalyst part based on the rhenium(I) complexes. Several kinds of peripheral and bridging ligands were used in the synthesis of the supramolecular structure, as shown in Figure 1. The photocatalytic activities of these supramolecules were strongly influenced by the choice of both the peripheral and the bridging ligands. Interesting results were obtained using the $bpyC_3bpy$ complexes **d_2Ru−Re** with the dmb peripheral ligands and **$RuRe_3$** as photocatalyst. Features include high selectivity of production of CO over H_2, relatively high quantum yields, and a surprisingly large turnover number for CO formation. In contrast, the binuclear complexes with the mfibpy bridging ligand or the $(CF_3)_2bpy$ peripheral ligands had much lower photocata-

(20) (a) Vlcek, A. A.; Dosdworth, E. S.; Pietro, W. J.; Lever, A. B. P. *Inorg. Chem.* **1995**, *34*, 1906. (b) Barigelletti, F.; Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 4115.

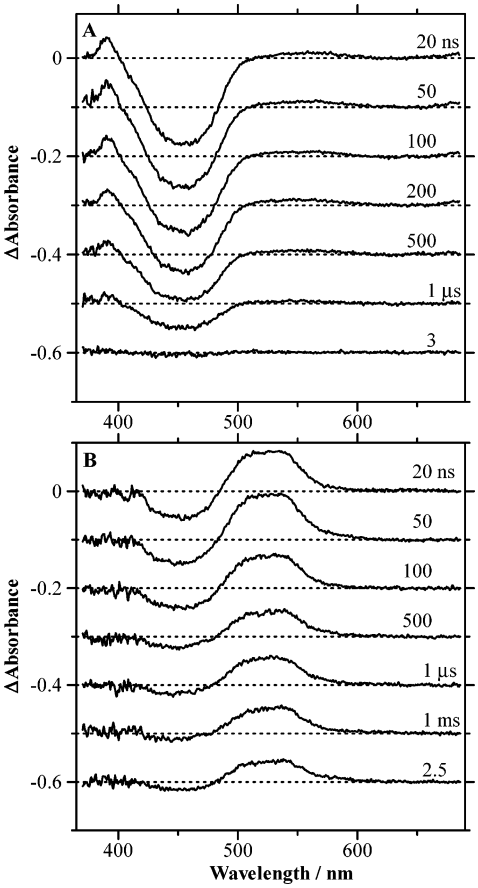
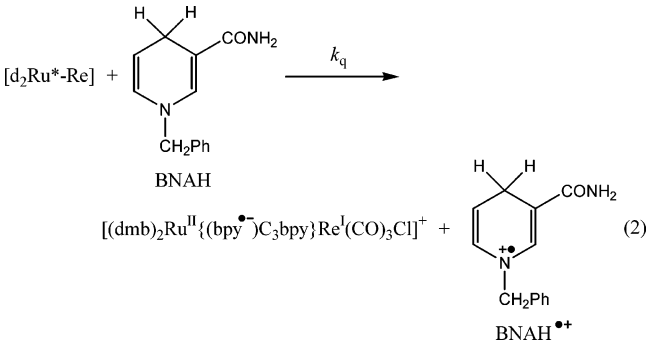


Figure 5. Time-resolved transient absorption spectra of **d_2Ru−Re** (A) without and (B) with the sacrificial reagent ([BNAH] = 0.1 M) in argon-saturated DMF at room temperature (λ_{ex} = 532 nm).

lytic activity or none. Even replacement of the dmb ligands by bpy (**b_2Ru−Re**) caused a dramatic decrease in TN_{CO}, as shown in Figure 2. Why are the photocatalytic abilities of these supramolecules so sensitive to the ligands? The answer will provide important information for designing new supramolecules with improved catalytic ability.

Mechanism of Photocatalytic Reaction. The ^{3}MLCT excited state of the ruthenium moiety in all of Ru−Re supramolecular complexes was efficiently quenched by BNAH when the excitation wavelength corresponded to the absorption regions of the Ru moiety ($\lambda \geq 470$ nm). Table 1 shows the quenching rates (k_q), calculated from linear Stern−Volmer plots and lifetimes of the luminescence from the ^{3}MLCT excited state, and the quenched fractions of the ^{3}MLCT excited state (η_q), obtained in the presence of 0.1 M BNAH. The quenching process should be reductive, since generation of the one-electron-reduced (OER) species of the Ru moiety was confirmed by transient absorption spectroscopy. As an example, Figure 5 shows the transient absorption (TA) spectra of the **d_2Ru−Re** in DMF. In the absence of BNAH, TA spectra showed positive absorption at $\lambda <$ 400 nm and strong bleaching centered at 460 nm, which is typical of the formation of the ^{3}MLCT excited state of Ru(II) polypyridine complexes with characteristic transitions within the polypyridine radical anion and the disappearance of the ground-state MLCT band.[21] The absorption decayed completely via first-order kinetics ($k = 1.1 \times 10^6$ s^{-1}), consistent with the decay rate of the emission (Figure 5A). In the presence of BNAH, new spectral features developed in the TA spectra: depletion of the ground-state MLCT band at 455 nm and an intense absorption at 480−580 nm, as shown in Figure 5B. These spectral features were also observed in a spectrum obtained from the continuous photolysis (λ_{ex} = 480 nm) of a DMF solution containing $[Ru(dmb)_3]^{2+}$ and BNAH (0.1 M) under argon atmosphere (Figure 6A). These spectra are very similar to that of $[Ru(bpy)_2(bpy^{\bullet-})]^+$ obtained by controlled electrochemical reduction of $[Ru(bpy)_3]^{2+}$ in dimethyl sulfoxide.[22] Therefore, it is very likely that the added electron resides on the Ru-bound bpy end of the bridging ligand bpyC_3bpy and the charge distribution is $[(dmb)_2Ru^{II}\{(bpy^{\bullet-})C_3bpy\}Re^{I}(CO)_3Cl]^+$, which is probably equilibrated with $[(dmb^{\bullet-})(dmb)Ru^{II}(bpyC_3bpy)Re^{I}(CO)_3Cl]^+$. The OER species of the Re moiety was not detected in a time-resolved IR spectrum obtained immediately after a laser flash into a DMF solution of **d_2Ru−Re** containing BNAH and TEA.[23,24] From these results, initiation processes of the **d_2Ru−Re**-photocatalyzed CO_2 reduction can be deduced, as in eqs 1 and 2.

$$[(dmb)_2Ru^{II}(bpyC_3bpy)Re^{I}(CO)_3Cl]^{2+} \xrightarrow{h\nu} \underset{\mathbf{d_2Ru-Re}}{} [(dmb)_2Ru^{III}\{(bpy^{\bullet-})C_3bpy\}Re^{I}(CO)_3Cl]^{+} \quad (1)$$
$$[\mathbf{d_2Ru^*-Re}]$$



(2)

The other additive TEOA could not quench the ^{3}MLCT excited state of [**d_2Ru*−Re**] at all, while it has been often

(21) (a) Braterman, P. S.; Harriman, A.; Heath, G. A.; Yellowless, L. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1801. (b) Gholamkhass, B.; Nozaki, K.; Ohno, T. *J. Phys. Chem. B* **1997**, *101*, 9010.

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(23) The ν_{CO} bands in the OER species of the Re complex $[Re(bpy^{\bullet-})(CO)_3\{P(OEt)_3\}]$ were observed at ~50 cm^{-1} lower energy than those of the original form $[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$, because of the stronger π-back-donation from the Re(I) dπ orbital to the ligand π^* one; see for example: Ishitani, O.; George, M. W.; Ibusuki, T.; Johnson, F. P. A.; Koike, K.; Nozaki, K.; Pac, C.; Turner, J. J.; Westwell, J. R. *Inorg. Chem.* **1994**, *33*, 4712.

(24) Time-resolved IR spectroscopy has been applied to several issues related to excited states and electronic structure in polypyridine complexes containing carbonyl ligands; see for example: (a) Dattelbaum, D. M.; Omberg, K. M.; Schoonover, J. R.; Martin, R. L.; Meyer, T. J. *Inorg. Chem.* **2002**, *41*, 6071. (b) Koike, K.; Okoshi, N.; Hori, H.; Takeuchi, K.; Ishitani, O.; Tsubaki, H.; Clark, I. P.; George, M. W.; Johnson, F. P. A.; Turner, J. J. *J. Am. Chem. Soc.* **2002**, *124*, 11448. (c) George, M. W.; Poliakoff, M.; Turner, J. J. *Analyst* **1994**, *119*, 551.

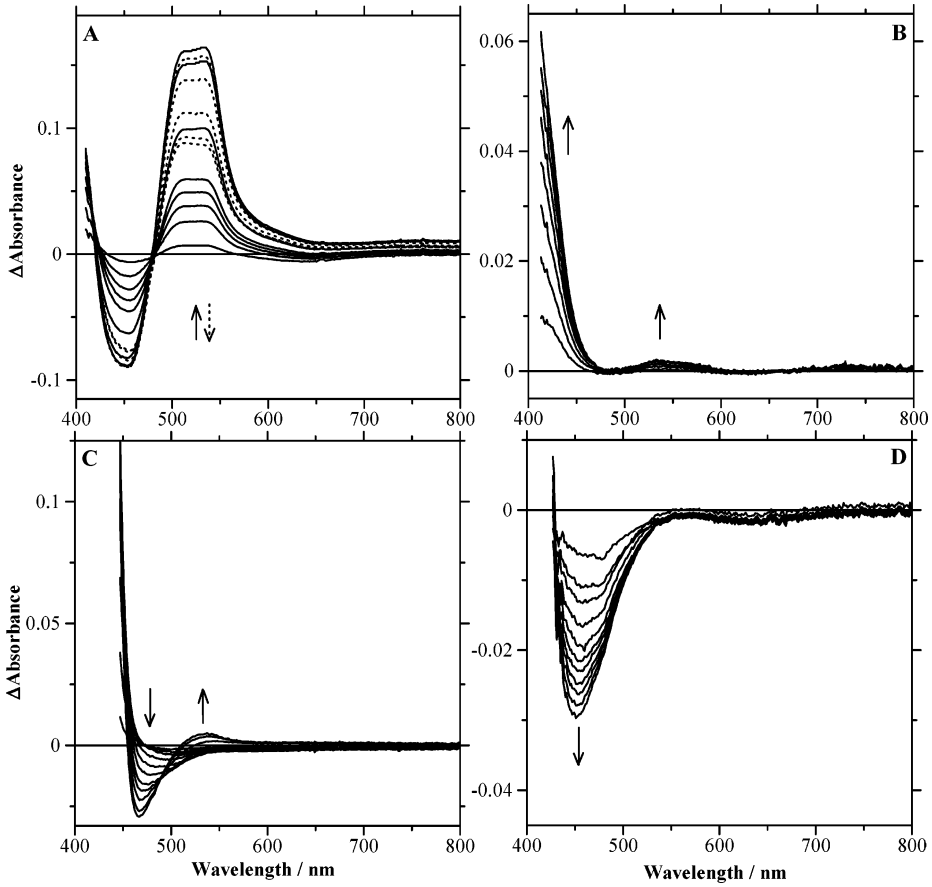
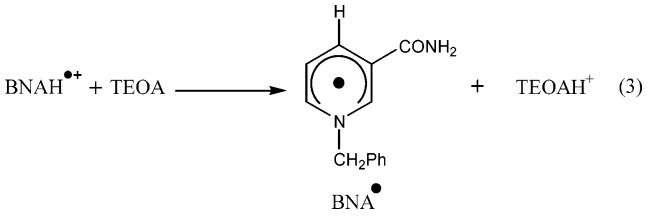


Figure 6. Steady-state measurement of the change in absorption spectra of argon-saturated DMF/TEOA/BNAH (0.1 M) solutions of (A) $[Ru(dmb)_3](PF_6)_2$ (λ_{ex} = 480 nm, 15 s intervals), (B) $[(dmb)Re(CO)_3Cl]$ (λ_{ex} = 365 nm, 5 min intervals), and (C) **d_2Ru−Re** (λ_{ex} = 480 nm, 10 s intervals). (D) is the same as (C) except that the solution is saturated with CO_2.

used as a sacrificial electron donor in metallic systems.[25] Lack of TEOA, however, slowed the photocatalytic CO_2 reduction. It has been reported that deprotonation of $BNAH^{\bullet+}$ is accelerated in the presence of the base.[26] TEOA should therefore play a role as a base to inhibit back electron transfer from $[(dmb)_2Ru^{II}\{(bpy^{\bullet-})C_3bpy\}Re^{I}(CO)_3Cl]^+$ to $BNAH^{\bullet+}$, as in eq 3. Following light irradiation, the oxidized dimers



of BNAH, produced by coupling of BNA•, were confirmed by ESI-MS measurement as in $[(BNA)_2]^+$ (m/z = 425).

As seen in Figure 5B, transient features due to the OER species, i.e., $[(dmb)_2Ru^{II}\{(bpy^{\bullet-})C_3bpy\}Re^{I}(CO)_3Cl]^+$, lasted up to 2.5 ms. This experiment was followed by continuous photolysis under argon or CO_2 atmosphere. Figure 6B,C show absorption spectra changes obtained for the continuous photolysis under argon of a DMF solution containing either $[(dmb)Re(CO)_3Cl]$ or **d_2Ru−Re** in the presence of both BNAH and TEOA. In the former (λ_{ex} = 365 nm), the OER species $[(dmb^{\bullet-})Re^{I}(CO)_3Cl]$ became detectable within several minutes from its weak but distinct absorption around 530 nm.[8,23,27] In the latter, 530-nm absorption was also detected within a similar time scale. In this case, although depletion of the ground-state MLCT band was observed, the Δ absorbance had a much smaller absolute value than for $[Ru(dmb)_3]^{2+}$ (Figure 6A), for which the spectrum corresponds to the OER species of Ru moiety. Since the spectra (Figure 6A,C) are not similar as expected if the same species were involved, the depletion is attributed to decomposition of a small amount of the Ru moiety. These data strongly suggest that the absorption around 530 nm observed during continuous irradiation of **d_2Ru−Re** (Figure 6C) is due to

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(27) (a) Kalyanasundaram, K. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2401. (b) Kutal, C.; Weber, M. A.; Ferraudi, G.; Geiger, D. *Organometallics* **1985**, *4*, 2161. (c) Kutal, C.; Corbin, A. J.; Ferraudi, G. *Organometallics* **1987**, *6*, 553.

the OER species of the Re moiety, i.e., $[(dmb)_2Ru^{II}\{bpyC_3(bpy\bullet^-)\}Re^I(CO)_3Cl]^+$. Since the excitation wavelength of 480 nm or longer cannot excite the Re moiety, appearance of the reduced Re moiety must be interpreted in terms of intramolecular electron transfer from the reduced Ru-bound bpy to the Re site, as shown in eq 4.

$$[(dmb)_2Ru^{II}\{(bpy\bullet^-)C_3bpy\}Re^I(CO)_3Cl]^+ \rightarrow [(dmb)_2Ru^{II}\{bpyC_3(bpy\bullet^-)\}Re^I(CO)_3Cl]^+ \quad (4)$$

This intramolecular electron transfer in the ground state should proceed at an exchange rate ($\Delta G = 0$), since the first reduction potential of the Re moiety ($E_{1/2} = -1.77$ V) is equal to that of the Ru moiety (Table 3). It has been reported that the OER of $[(bpy)Re(CO)_3Cl]$ reacts with CO_2 via a ligand loss process within several seconds to give CO.[28] It is reasonable to suppose that $[(dmb)_2Ru^{II}\{bpyC_3(bpy\bullet^-)\}Re^I(CO)_3Cl]^+$ reacts with CO_2 via Cl^- loss at a similar rate. ESI-MS analysis of the reaction products showed that the Cl^- ligand in the diad was partially released during the photocatalytic reaction. It follows that reduction of CO_2 with the OER species of the Re moiety is the rate-determining process in the photocatalytic reduction of CO_2 by **d_2Ru−Re**. This is an important reason **d_2Ru−Re**, and probably **$RuRe_3$**, can act as efficient supramolecular photocatalysts for CO_2 reduction, even though intramolecular electron transfer from the photosensitizer Ru moiety to the catalyst Re moiety is relatively slow. We are unable to follow reactions occurring on time scales greater than 2.5 ms by TA or greater than 100 ms by time-resolved IR spectroscopies,[23] so that we can state only that intramolecular electron transfer is a relatively slow process that takes several hundred milliseconds to a second.

The following section discusses the molecular architecture necessary for constructing supramolecular photocatalysts using both the information described above and a comparison with the results of other systems.

Architectural Requirement. A detailed comparison of the photocatalytic activities of the binuclear complexes with the $bpyC_3bpy$ bridging ligand, i.e., **tfbRu−Re**, **b_2Ru−Re**, and **d_2Ru−Re**, clearly shows that, to design a supramolecule that efficiently photocatalyzes reduction of CO_2, electron transfer from the photosensitizer Ru site to the catalyst Re site must not be endothermic. In the cases of **tfbRu−Re** and **b_2Ru−Re**, the production of OER species of the Re moiety is not favored energetically, because the intramolecular electron transfer is endothermic ($\Delta G = +0.55$ and $+0.05$ eV, respectively). In the photocatalytic reaction using **tfbRu−Re**, the OER species $[\{(CF_3)_2bpy\}\{(CF_3)_2bpy\bullet^-\}Ru^{II}(bpyC_3bpy)Re^I(CO)_3Cl]^+$ was indeed accumulated in the solution, but only a small amount of CO was produced. Although the difference in the endothermicity of the electron transfer between **b_2Ru−Re** and **d_2Ru−Re** is very small (only $+0.05$ eV), the photocatalytic activity of **b_2Ru−Re** is much lower than that of **d_2Ru−Re**. Therefore, as well as the energetic aspect, electron localization on the bridging ligand seems to be a further decisive factor in view of the required function of the electron transfer between the subunits.

The nature of the bridging ligand itself plays a fundamental role in defining the electrochemical and spectroscopic properties of the supramolecular systems. For **Ru(mfibpy)-Re** and **Re(mfibpy)Ru**, although the requirement of bridging-ligand localization of the electron is satisfied, their photocatalytic abilities are low. Estimation of the free energy change is difficult in these binuclear complexes. We can assume that, in the case of **Ru(mfibpy)Re**, the electron is mainly localized on the Ru end of the bridging ligand, because the energy level of the π^* orbital on the phenanthroline−imidazolyl motif of mfibpy is lower than that on the bpy one coordinating to the Re. It follows that the low electron density on the catalytic Re site in the OER species must be a principal reason for the low photocatalytic activity of **Ru(mfibpy)Re**. In the case of **Re(mfibpy)Ru**, in contrast, electron localization must be on the Re site, which would give rise to its good photocatalysis. We have reported that photocatalyses of the mononuclear complexes *fac*-$[Re(LL)(CO)_3(PR_3)]^+$, where LL and R are respectively a diimine ligand and an alkyl group, depend strongly on their reduction potentials $E_{1/2}^{red}(LL/LL\bullet^-)$, and an efficient photocatalytic reduction of CO_2 requires $E_{1/2}^{red}(LL/LL\bullet^-) < -1.41$ V vs Ag/Ag^+.[8c] In view of the wide conjugation of the mfibpy and the strong electronic communication across the bridging ligand, the reducing power of the OER species ($E_{1/2}^{red} = -1.1$ V vs Ag/Ag^+) should be insufficient for efficient reduction of CO_2 under these conditions.

The strong electronic communication between the photosensitizer moiety and the catalyst moiety through the bridging ligand lessens the photocatalytic activity even though it accelerates the electron transfer between them. This fact should be an important general guide for constructing supramolecular systems to act as photocatalyst in CO_2 reduction. Electron transfer must occur from the reduced photosensitizer to the catalyst site, but this does not need to be a rapid process. This is because the following step, i.e., reaction of the OER species of the catalyst site with CO_2, is usually slower.[8c,28,29] In the case of the good photocatalyst **d_2Ru−Re**, for example, the electron transfer proceeded at a time scale of several hundred milliseconds to seconds. The reducing power of the OER species of the catalyst site must be maintained as strong as possible, because it is the dominating factor determining the overall reaction rate of the OER species with CO_2. Therefore, widely conjugated bridging ligands are not suitable for supramolecular photocatalysts of CO_2 reduction, since their π^* energy levels are lower than those of the corresponding nonconjugated ligands.

The formation of CO requires injection of one more electron into the reaction product(s) of the OER species with CO_2 (CO_2 adduct). Participation of BNA• is unlikely in view

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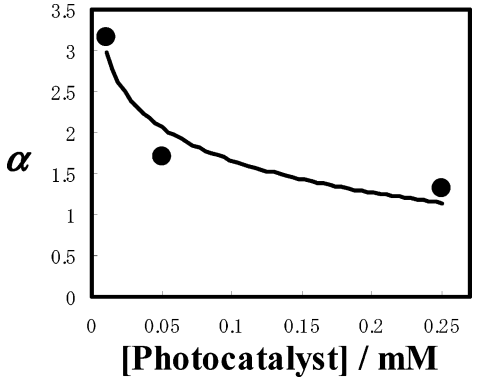

Figure 7. Concentration dependence of the relative TN_{CO} in the binuclear complex of $\mathbf{d_2Ru-Re}$ with respect to a 1:1 mixture of $[Ru(dmb)_3]^{2+}$ and $[(dmb)Re(CO)_3Cl]$ ($\alpha = TN_{CO}(bi)/TN_{CO}(mono's)$).

of its rapid dimerization to give BNA_2's,[30] which were detected in the solutions after the photocatalytic reactions. The possible candidates are therefore the OER of the Ru moiety produced by second photochemical electron transfer from another BNAH or another OER species of the starting complex. Figure 7 shows the concentration dependence of the relative TN_{CO} in the binuclear complex of $\mathbf{d_2Ru-Re}$ with respect to 1:1 mixture of mononuclear complexes, $[Ru(dmb)_3]^{2+}$ and $[(dmb)Re(CO)_3Cl]$, where $\alpha = TN_{CO}(bi)/TN_{CO}(mono's)$. At progressively lower concentrations, the binuclear system gained in superiority over the mixed mononuclear one. The proximity effect between the Ru and Re moiety in the supramolecule probably suppresses decomposition of the CO_2 adduct prior to injection of the second electron. A more dramatic proximity effect was observed by comparing $\mathbf{RuRe_3}$ with a 1:3 mixture of $[Ru(dmb)_3]^{2+}$ and $[(dmb)Re(CO)_3Cl]$, as shown in Figure 2. Moreover, the lower TN_{CO} observed for the 1:3 mixture than the 1:1 mixture suggests that, in the mixed mononuclear system, the greater probability of capturing an electron from the OER species of $[Ru(dmb^{\bullet-})(dmb)_2]^{2+}$ by $[(dmb)Re(CO)_3Cl]$ hampers the second electron transfer to the already formed CO_2 adduct. In the supramolecular system $\mathbf{RuRe_3}$, no such decrease in TN_{CO} was observed, probably because the Ru moiety is always close to the CO_2 adduct, which could have greater oxidation power than the other Re moieties.

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Conclusion

Enhancement of the photocatalytic response to light in the visible region is achieved by fabricating supramolecules featuring covalently linked ruthenium and rhenium moieties. The greatly improved photocatalytic activity in the case of the tetranuclear complex $\mathbf{RuRe_3}$ and the binuclear complex $\mathbf{d_2Ru-Re}$ is attributed to intramolecular electron transfer, from the OER species $[(dmb)_2Ru^{II}\{(bpy)^{\bullet-}C_3bpy\}Re^{I}(CO)_3Cl]^+$ produced following the selective excitation and subsequent reductive quenching of the Ru ^{3}MLCT excited state, to the Re moiety.

These results provide new information on the electrochemical and structural requirements needed to build supramolecular metal complexes which can be used as an efficient photocatalyst for CO_2 reduction. Future studies will focus on the design and application of new multinuclear metal complexes.

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