Bridging Efficiency within Multinuclear Homogeneous Catalysts in the Photocatalytic Reduction of Carbon Dioxide

Simon Meister, Richard O. Reithmeier, Alexander Ogrodnik, and Bernhard Rieger*^[a]

A trinuclear complex consisting of one $[Ru(dmb)_3]^{2+}$ (dmb = 4,4'-dimethyl-2,2'-bipyridine) (**Ru**) and two $[Re(dmb)(CO)_3CI]$ (**Re**) building blocks, $[Re(CO)_3CI(dmb-dmb)Ru(dmb)(dmb-dmb)Re(CO)_3CI](PF_6)_2$ (**Re-Ru-Re**), is presented. Photophysical properties of **Re-Ru-Re** and the individual components with different or no covalent linkages are thoroughly investigated and compared. To elucidate the role of the single covalent bonds, photocatalytic reduction of CO₂ is performed with the trinuclear complex and a series of model systems featuring systematic absence of linkages between the metal centers. Photoluminescence spectra and quantum yields reveal efficient

Introduction

Photocatalysis has emerged as an elegant methodology for energetically disfavored reactions.^[1] It has become a viable approach for the production of solar fuels, paving the way for the valorization of $H_2O^{[2]}$ or CO_2 .^[3] The latter has proven useful as an alternative and sustainable C1 feedstock, especially if the reduction of CO₂ allows for the exploitation of established synthetic pathways.^[4] The selective reduction of CO₂ to CO can be performed with Re^I catalysts, as reported by Hawecker, Lehn, and Ziessel in the early 1980s.^[5] These complexes of the general formula [Re(NN)(CO)₃X] (NN = α, α' -dipyridyl or phenanthroline; $X = CI^{-}$, Br^{-} , or SCN^{-}) are able to act as photosensitizer, oxidation site, and reduction site all at once. After excitation, a sacrificial amine [typically triethanolamine (TEOA) or triethylamine] is oxidized and an electron transferred to CO2.^[6] Recently, our group was able to show that TEOA radicals and excessive irradiation contribute to catalyst deactivation, accounting for low turnovers and poor catalyst stability.^[7] One approach to enhance catalytic performance is the separation of photosensitizer, oxidation site, and reduction site. This may be achieved by using Ru^{II} complexes as photosensitizer and oxidation site, for example, leaving the task of selective CO₂ reduction to the Re¹ catalyst.^[8] Major improvements are observed in terms of turnovers and stability if mixed Re^I/Ru^{II} catalytic systems with 1-benzyl-1,4-dihydronicotinamide (BNAH) as sacrificial amine and CO₂ as electron acceptor are used.^[9] In this type of system, energy transfer from the excited state of **Re** to **Ru** if these fragments are covalently linked. Moreover, intramolecular electron transfer from the one-electron reduced species of **Ru** to **Re** occurs if there is covalent bonding, leading to a higher photostability and thus the highest turnover number in photocatalytic CO₂ reduction of 199 for the trinuclear complex **Re**–**Ru**–**Re** within the systems under investigation. Optimized experimental conditions reveal the highest turnover number (315) reported to date for Re¹/Ru^{II}-based homogeneous catalysts in photocatalytic CO₂ reduction.

the Ru moiety is typically excited and subsequently reduced by BNAH, followed by electron transfer from the reduced Ru complex to the Re catalyst, where CO₂ reduction takes place. Several attempts have been made to further increase catalytic performance by covalently linking oxidation and reduction sites^[9,10] and by connecting two reduction sites.^[11] In both cases, the length of the linker was revealed to govern the turnover number (TON) and turnover frequency (TOF). It was found that an ethyl tether between two reduction catalysts promoted a binuclear mechanism, whereas the same linker between a reduction and an oxidation site facilitated electron transfer from BNAH to CO₂, increasing both TON and TOF. Interestingly, conjugated linkers were found to be unsuitable in CO₂ reduction, although a more efficient electron transfer would be expected. In fact, the electronic properties of the complexes were changed in such a way that catalytic performance deteriorated.^[10c] Consequently, it can be concluded that the ideal photocatalyst for CO₂ reduction should consist of at least one photosensitizer unit and two reduction sites, which are all in spatial proximity and connected by short alkyl chains to support fast electron transfer and a binuclear mechanism. Our focus was to determine which covalent bond was crucial for efficient CO₂ reduction. However, the wide range of reaction conditions and catalytic setups rendered comparison of different studies difficult. Herein, we present four similar trinuclear catalytic systems, each of them consisting of two [Re(dmb)(CO)₃Cl] (dmb = 4,4'dimethyl-2,2'-bipyridine) reduction catalysts and one [Ru(dmb)₃]²⁺ photosensitizer and oxidation site, differing only in the way these centers are covalently linked (Figure 1). Photophysical properties of the trinuclear systems and their single components were investigated in detail and photocatalytic re-

 [[]a] S. Meister, R. O. Reithmeier, Dr. A. Ogrodnik, Prof. Dr. B. Rieger Wacker Lehrstuhl für Makromolekulare Chemie TU München - Technische Chemie Lichtenbergstr. 4, 85748 Garching (Germany)

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Figure 1. Model systems used for CO₂ reduction incorporating two Re¹ centers and one Ru^{II} center with different bridging modes.

duction of CO₂ was performed to elucidate the relevance of each single covalent connection of the two metal centers.

Results and Discussion

Synthesis and characterization

The complexes $[\text{Re}(\text{dmb})(\text{CO})_3\text{CI}]$ $(\text{Re})^{[7]}$ and $[\text{Ru}(\text{dmb})_3](\text{PF}_6)_2$ $(\text{Ru})^{[12]}$ were prepared according to procedures previously reported in literature. $[\text{Re}(\text{CO})_3\text{CI}(\text{dmb}-\text{dmb})\text{Re}(\text{CO})_3\text{CI}]$ (Re-Re) was prepared following the procedure reported for the bromium derivative.^[11] A three-step synthesis for $[\text{Re}(\text{CO})_3\text{CI}(\text{dmb}-\text{dmb})\text{Ru}(\text{dmb})_2](\text{PF}_6)_2$ (Re-Ru) and the new trinuclear complex $[\text{Re}(\text{CO})_3\text{CI}(\text{dmb}-\text{dmb})\text{Ru}(\text{dmb})\text{Ru}(\text{dmb})(\text{dmb}-\text{dmb})\text{Re}(\text{CO})_3\text{CI}](\text{PF}_6)_2$

(Re-Ru-Re) was developed, which is shown for the latter in Scheme 1. The first step comprised the synthesis of [Re-

(CO)₃Cl(dmb-dmb)] for both complexes, after which the photosensitizer was assembled. For the synthesis of Re-Ru-Re, two equivalents of [Re(CO)₃Cl(dmb-dmb)] were brought to reaction with one equivalent of $[Ru(cod)Cl_2]_n$ (cod = 1,5-cyclooctadiene) in a microwave reactor with moderate irradiation (50 W), whereas for the synthesis of Re-Ru, dmb was used instead of [Re(CO)₃Cl(dmb-dmb)]. The exclusion of H₂O during this step prevented substitution of the chloro ligands at the Ru center.^[12] In the following step, MeOH was added to facilitate Cl⁻ dissociation and coordination of either dmb for the synthesis of Re-Ru-Re or [Re(CO)₃Cl(dmb-dmb)] for the synthesis of **Re**-Ru. Salt metathesis yielded the PF_6^- salts of the desired complexes. All complexes were characterized fully by using ¹H NMR, ESI-MS, and UV/Vis spectroscopies and elemental analysis. For the complexes containing carbonyl groups, IR spectra were recorded additionally (see the Experimental Section).



Scheme 1. Synthesis of the trinuclear complex Re–Ru–Re.



Photophysical properties

The metal centers in the bi- and trinuclear complexes **Re**–**Re**, **Re**–**Ru**, and **Re**–**Ru**–**Re** are connected by non-conjugated bridging ligands, which should hinder electronic communication between the metal centers in the electronic ground state.^[10c,13] This is confirmed in UV/Vis spectra of the complex mixtures **Re**+**Re**+**Ru**, **Re**–**Re**+**Ru**, **Re**–**Ru**+**Re**, and **Re**–**Ru**– **Re**, which strongly resemble one another (Figure 2). The spectra are of additive nature, that is, the absorbance at a given wavelength is identical to the sum of the absorbance of **Ru** and two times the absorbance of **Re**, indicating that electronic communication in the ground state does not occur. Absorption maxima and corresponding extinction coefficients are given in Table 1. Comparison with the spectra of isolated **Ru** or **Re** reveals that the broad absorption in the visible region at λ = 420–500 nm stems from the photosensitizer **Ru**, whereas the



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Figure 2. UV/Vis spectra of the four trinuclear model systems. Spectra of $\mathbf{Re} + \mathbf{Re}$ and \mathbf{Ru} are depicted for comparison.

Re moieties absorb only in the UV region up to $\lambda = 420$ nm. The lowest energy transitions with absorption maxima at $\lambda = 460$ nm (**Ru**) and $\lambda = 363$ nm (**Ru** and **Re**) can be assigned to metal-to-ligand charge transfer (MLCT; $d\pi \rightarrow \pi^*$), whereas the strong absorption in the UV range at $\lambda \approx 290$ nm is associated with intraligand processes $(\pi \rightarrow \pi^*)$.^[14]

normalized emission The spectra of the four trinuclear mixtures appear almost identical, with an emission maximum at $\lambda = 633-634$ nm (Table 1 and Figure 3). The spectra are dominated by a strong emission from Ru, which appears at a maximum of $\lambda = 633$ nm with a relatively high quantum yield (0.083). The contribution of **Re** with a maximum at $\lambda = 609$ nm is rather weak due to its low quantum yield (0.007) but still in a detectable range. In Figure 3, the nonnormalized spectra of isolated Re (50 µм) and Ru (25 µм) are displayed, showing their original relative intensities. Assuming the absence of electronic communication between the com**Table 1.** Photophysical data for the four trinuclear model systems and their single components including absorption (λ_{abs}) and emission (λ_{em}) maxima, Stern–Volmer constants (K_{SV}) , lifetimes of the excited states (τ) , quenching rate constants (k_Q) , and photoluminescence quantum yields (Φ_{em}) for Ru (if not stated otherwise) for excitation at $\lambda = 365$ and 520 nm.

System	[Re] ^[a]	[Ru] ^[a]	$\lambda_{abs}^{[b]}$	$\varepsilon^{[b]}$	$\lambda_{\rm em}^{\rm [b]}$	$K_{\rm SV}^{\rm [b]}$	$\tau^{\rm [b,c]}$	$k_{Q}^{[d]}$	$\varPhi_{\rm em}{}^{\rm [b,e]}$	$\varPhi_{\rm em}{}^{\rm [b,f]}$
	[µм]	[µм]	[nm]	[10 ³ м ⁻¹ cm ⁻¹]	[nm]	[M ⁻¹]	[ns]	$[M^{-1}NS^{-1}]$		
Re + Re + Ru	50	25	460	16.2	633	7923	879	9.01	0.065	0.085
			362	16.2						
			289	125.4						
Re-Re+Ru	50	25	460	17.3	633	8043	881	9.13	0.068	0.083
			363	16.6						
			289	132.6						
Re–Ru + Re	50	25	460	17.2	634	8183	892	9.17	0.103	0.090
			363	16.1						
			289	128.1						
Re-Ru-Re	50	25	460	16.5	634	8083	899	8.99	0.125	0.077
			363	16.5						
			290	119.9						
Re–Ru	25	25	462	17.1	634	7704	890	8.66	0.108	0.089
			361	11.9						
			289	107.7						
Re + Ru	25	25	461	16.5	633	8120	876	9.27	0.073	0.082
			360	12.0						
			289	107.9						
Ru	0	25	462	16.6	633	9104	888	10.25	0.083 ^[g]	0.083 ^[g]
			327	12.6						
			289	93.4						
Re	25	0	364	3.9	609	-	27 ^[h]	-	0.007 ^[i]	0.000 ^[i]
			291	14.8						

[a] Concentration of metal centers; [b] Measured in Ar-saturated DMF solution (ε = extinction coefficient); [c] Excitation with a short laser pulse (<15 ns) at λ = 355 nm; [d] Calculated from K_{sv} and τ ; [e] λ_{ex} = 365 nm; [f] λ_{ex} = 520 nm; [g] From Ref. [16c], converted for DMF as described in Ref. [17]; [h] From Ref. [6a] (in MeCN); [i] Quantum efficiencies for photoluminescence of Re.

plexes in the trinuclear mixture without covalent linkages, the calculated sum of the spectra of \mathbf{Ru} and $\mathbf{Re} + \mathbf{Re}$ should reflect the emission spectrum of $\mathbf{Re} + \mathbf{Re} + \mathbf{Ru}$. However, the emission intensity of $\mathbf{Re} + \mathbf{Re} + \mathbf{Ru}$ is lower than the calculated sum, but through normalization it is possible to superimpose the measured and calculated spectra (Figure S2). The loss of intensity correlates with a lower quantum yield for $\mathbf{Re} + \mathbf{Re} + \mathbf{Ru}$ com-

pared with **Ru**. This can be attributed to a filter effect: at the excitation wavelength (365 nm), a 50 μ M solution of **Re** (i.e., **Re** + **Re**) and a 25 μ M solution of **Ru** absorb approximately equally, causing the absorbance of **Re** + **Re** + **Ru** to be twice as high as that of the single components. Considering the logarithmic correlation between absorbance and absorption, the 25 μ M trinuclear mixture (50 μ M **Re** + 25 μ M **Ru**) absorbs less



Figure 3. Normalized photoluminescence spectra of the four trinuclear model systems (λ_{ex} = 365 nm, concentration = 25 μ M for every listed metal). Original (non-normalized) spectra for Re + Re and Ru are shown for comparison. Re + Re + Ru is normalized to the sum of Re + Re and Ru. Re–Re + Ru, Re–Ru + Re, and Re–Ru–Re are normalized to Re + Ru + Re and only differ from the sum of Re + Re and Ru in the region of λ = 500–580 nm.

than double (1.7-fold) the amount of photons compared with the 25 μ M solution of **Ru** or the 50 μ M solution of **Re**. Under the experimental conditions used in this study, only 83% of the respective complexes in the trinuclear mixture are excited compared with the homonuclear solutions (see the Supporting Information for detailed calculations), and thus emission intensity is somewhat lower.

For a better comparison, the emission spectra of the trinuclear mixtures are normalized to the calculated sum of $\mathbf{Re} + \mathbf{Re}$ and \mathbf{Ru} spectra in Figure 3. The actual quantum yields are given in Table 1 and non-normalized plots are shown in Figure S4. As mentioned above, superimposition is possible for the mixture without any covalent linkages (Figure S2). The other spectra show slight differences in the range of $\lambda = 500-580$ nm, suggesting decreasing emissions from the triplet MLCT (³MLCT) of **Re** in the order **Re**–**Re**+**Ru**>**Re**–**Ru**+**Re**> **Re**–**Ru**–**Re**. The emission spectrum of **Re**–**Ru**–**Re** can be super-

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imposed with that of pure Ru, indicating that no emission from Re in the trinuclear complex occurs (Figure S3). However, with decreasing emissions from Re, quantum yields increase, which is only feasible if energy transfer from excited Re to Ru occurs. A similar phenomenon has been observed before in a related complex.^[15] Consequently, covalent linkage of Re and ${\bf R}{\bf u}$ enhances production of the ${\bf R}{\bf u}$ 3MLCT state because ${\rm Re}^{\rm I}$ moieties act as light antennae if irradiation is performed with UV or blue light. To further substantiate the proposed energy transfer mechanism, the determination of quantum yields was repeated by using green light ($\lambda = 520$ nm) for the excitation of the complexes. Therein, quantum yields should no longer be affected by energy transfer from Re to Ru because Re cannot be excited. As expected, quantum yields are identical for all mixtures within the range of error (Table 1). Deviations might be a result of imprecise integration of emission signals due to overlapping of excitation ($\lambda = 520$ nm) and emission $(\lambda = 633 \text{ nm})$ wavelengths (Figure S5).

Photoluminescence is quenched efficiently with BNAH. Stern–Volmer plots reveal very similar Stern–Volmer constants (K_{SV}) for all four systems under investigation (Figure 4). The life-



Figure 4. Stern–Volmer plots of deoxygenated DMF solutions of the four trinuclear model systems. λ_{ex} = 365 nm, quencher (Q) = BNAH.

times (τ) of the excited states range between 880 and 900 ns, which corresponds to the ³MLCT lifetime of **Ru**.^[14b, 16] The decay of photoluminescence is shown exemplarily for **Re**—**Ru**—**Re** in Figure 5. Apparently, covalent linkage of the complexes does not influence quenching efficiency [with respect to the quenching rate constant (k_Q)], which is reflected in similar K_{SV} and τ values (Table 1). Stern–Volmer plots of all systems listed in Table 1 are presented in the Supporting Information (Figure S8).

Catalytic performance

The trinuclear mixtures presented in Figure 1 were tested in photocatalytic CO_2 reduction to evaluate the impact of covalent linkages between each of the single complexes. In mixed





Figure 5. Decay of photoluminescence after excitation of complex Re–Ru–Re with a short laser pulse (<15 ns) at λ =355 nm.

Re^I/Ru^{II} systems with BNAH as sacrificial electron donor and irradiation in the visible range above $\lambda = 500$ nm, Ru is reduced typically after excitation, producing a one-electron reduced (OER) species. Subsequently, the OER species of Re is built through inter- or intramolecular electron transfer and CO₂ reduction takes place at the Re catalyst.^[9] Usually, TEOA is added in addition to BNAH to deprotonate the oxidized BNAH and thus prevent electron back-transfer.^[9,15a] For the photocatalytic experiments, the respective model system (Figure 1) was dissolved in DMF (0.03 mм), BNAH (0.1 м) and TEOA (1.7 м) were added, and the solution was saturated with CO₂ and irradiated under ambient conditions with an LED light source emitting at $\lambda =$ 520 nm. The systems under investigation showed moderate to good activity during the first hour of irradiation (Figure 6). Deterioration during the second hour of irradiation was due to degeneration of the photosensitizer Ru, which was confirmed by experimental results from the periodic addition of Ru (Figure S6).

As expected, the system with the mononuclear mixture $(\mathbf{Re} + \mathbf{Re} + \mathbf{Ru})$ shows the lowest activity and stability, illustrat-



Figure 6. Time vs. conversion plots of the four trinuclear model systems (0.03 mm). Turnovers were calculated based on Ru content in each mixture. Irradiation was performed at $\lambda = 520$ nm.

ed by a moderate TOF (1.3 min⁻¹) and TON (40) (Table 2). Connecting the Re^I centers (**Re**–**Re** + **Ru**) causes an approximately threefold increase in both TOF (3.8 min⁻¹) and TON (129). CO₂ reduction at the Re catalyst is known to be rate-limiting in

Table 2. TOFs and TONs of the four trinuclear model systems (0.03 mm) in CO₂-saturated DMF solution with BNAH (0.1 m) and TEOA (1.7 m). Values were calculated per Ru^{II} center (for each mixture). Irradiation was performed at $\lambda = 520$ nm.

System	TOF [min ⁻¹]	TON			
Re + Re + Ru	1.3	40			
Re–Re + Ru	3.8	129			
Re–Ru + Re	4.3	174			
Re-Ru-Re	4.2	199			
Re-Ru-Re ^[a]	n.d.	315			
[a] 0.05 mm irradiation intensity reduced to 2.5% compared to all other					

 $[a]\,0.05\,\,\text{m}\textsc{m}$, irradiation intensity reduced to 2.5% compared to all other experiments.

such systems.^[9] Owing to the limited stability of the photosensitizer, it is crucial how fast CO₂ is converted at the Re moiety. Apparently, the binuclear CO₂ reduction mechanism, which emerges if Re^I centers are forced into spatial proximity,^[11] contributes significantly to acceleration of the CO₂ reduction process, even in mixed Re^I/Ru^{II} systems. Thus, in the timeframe during which active photosensitizer is present (i.e., before degeneration), more CO can be produced in the presence of the faster reduction catalyst Re-Re. However, a larger effect on catalyst performance is observed if photosensitizer (Ru) and reduction catalyst (Re) are covalently linked. The activity (TOF) reaches a rate of 4.2–4.3 min⁻¹ for both Re-Ru + Re and Re-Ru-Re. Interestingly, the rate increase by enabling intramolecular electron transfer from Ru to Re, which is possible through the ethyl bridge,^[10a] seems to be independent of the number of Re sites connected to the same Ru center. Similar TOFs for both **Re–Ru + Re** and **Re–Ru–Re** suggest that the Re moieties in **Re–Ru–Re** are not close enough to promote binuclear CO₂ reduction. Nevertheless, the contribution from intramolecular electron transfer to the overall activity is slightly larger than the contribution from the binuclear mechanism, reflected in a higher TOF for Re-Ru + Re (4.3 min⁻¹) than for Re-Re + Ru(3.8 min⁻¹). Notably, domination of the binuclear mechanism can be excluded for Re-Ru + Re because there is no spatial proximity between the Re centers. Regarding catalyst longterm stability, the TON can be increased by connecting more Re sites to the photosensitizer, resulting in up to 200 turnovers for the trinuclear catalyst under these conditions. Covalent linkage of reduction catalysts to the photosensitizer enhances electron transfer from Ru to Re, thus decreasing the lifetime of the reduced state at Ru (OER).^[9] As reported before for Re^I catalysts and proposed for other photocatalysts, degeneration of the catalyst by excitation of the OER species is possible.^[7] This is considered to be the main deactivation route for the degeneration of the photosensitizer. Therefore, shortening the lifetime of the OER photosensitizer accounts for higher catalyst stability and increasing TONs. Consequently, the new catalyst

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Re–Ru–Re is found to be the catalyst with the best performance within the systems under investigation.

To further increase the TON of the most active catalytic system, experimental conditions were varied. Assuming that CO₂ reduction at the Re^I moiety is still rate-limiting in the trinuclear catalyst Re-Ru-Re and taking into account recently published results, it should be possible to further increase the TON if a lower irradiation intensity is applied.^[7] Thereby, the OER photosensitizer will be less prone to degeneration through excess irradiation, with excitation being still sufficient to generate the OER species. In the following experiment, only 2.5% of the original irradiation intensity was used. For comparability with other research groups' results, catalyst concentration was adjusted to 0.05 mm. After 16 h of irradiation, the TON reached 244, exceeding those of comparable catalysts comprising covalently linked Re¹/Ru^{II} complexes.^[9, 10, 15a, 18] Further irradiation revealed ongoing activity for more than 24 h, resulting in a final TON of 315, the highest TON reported to date for Re¹/Ru¹¹based catalysts (Figure S7).

Conclusions

rhenium(I)/ruthenium(II) А new trinuclear complex [Re(CO)₃Cl(dmb–dmb)Ru(dmb)(dmb–dmb)Re(CO)₃Cl](PF₆)₂ (Re-Ru-Re; dmb=4,4'-dimethyl-2,2'-bipyridine) has been synthesized and its photophysical properties investigated thoroughly. Its photocatalytic activity in carbon dioxide reduction was studied and compared to similar systems, in which different modes of covalent linkage of the ruthenium and rhenium centers were present. Thereby, the effect of every covalent link between two or more complexes was revealed. Owing to slow carbon dioxide reduction at the rhenium catalyst coinciding with a fast degeneration of the ruthenium-based photosensitizer, it was found that connecting two reduction catalysts enhanced photocatalytic performance in mixed rhenium(I)/ruthenium(II) systems. This was attributed to a binuclear reduction mechanism, which promoted faster carbon dioxide reduction. However, covalent linkage of reduction catalyst and photosensitizer was found to be slightly more relevant to yield higher turnover frequencies and numbers (TONs) because intramolecular electron transfer was enabled. This accounted for a reduced lifetime of the one-electron reduced photosensitizer, rendering the system less prone to deactivation as a result of photobleaching by excitation of the reduced photosensitizer. Consequently, the new trinuclear complex Re-Ru-Re was found to be the catalyst with the highest TON (199) within the four systems under investigation. Optimized experimental conditions afforded the highest TON (315) reported to date for rhenium(I)/ruthenium(II) mixed catalytic systems.

Moreover, an interesting phenomenon was observed in the study of photoluminescence spectra and quantum yields: excitation of the trinuclear complex **Re**—**Ru**—**Re** with UV light resulted in very efficient triplet–triplet energy transfer from the triplet metal-to-ligand charge transfer of **Re** to **Ru**. Thus, besides promoting an intramolecular electron transfer from the one-electron reduced species of **Ru** to **Re**, the covalent connection of rhenium moieties enabled them to act as light antennae. This is an important property, considering that many light sources (including the sun) emit in the visible and UV regions. Efficient multinuclear photocatalysts should be able to use any part of the catalyst for the absorption process and reactions should be limited to a defined catalytic site to achieve high selectivity. Thus, energy and electron transfer are two important parameters, whose optimization is crucial for catalyst performance. The presented trinuclear catalyst combines electron and energy transfer between the respective catalytic sites perfectly, with potential for efficient performance over a broad irradiation spectrum. However, triethanolamine would have to be substituted by a base that does not quench the excited states of rhenium and ruthenium. Studies with irradiation at various wavelengths using a different base are the subject of further investigations in our laboratories.

Experimental Section

Instrumentation and measurements

All manipulations were performed by using standard Schlenk techniques if not stated otherwise. ¹H NMR and ¹³C NMR spectra were measured on a Bruker AVIII-300 spectrometer at 298 K and referenced to residual solvent signals.^[19] IR spectroscopy was performed on a Bruker Vertex-70 FTIR spectrometer at RT in bulk material. ESI-MS spectra were recorded on a Varian LC-MS 500 spectrometer. UV/Vis spectra were measured on a Varian Cary 50 spectrophotometer in a UV quartz cuvette (10 or 1 mm). Emission spectra were measured on an Avantes Avaspec-2048 spectrometer at 25°C by using a Prizmatix Mic-LED-365 for excitation at $\lambda = 365$ nm or a Luxeon K2 Emitter LED for excitation at $\lambda =$ 520 nm. Photoluminescence quantum yields were determined relative to the standard $[Ru(dmb)_3](PF_6)_2$ ($\Phi_{em} = 0.083$); for a detailed description, see the Supporting Information.^[16c, 17] Lifetimes of the excited states were determined by fitting the exponential decay of the photoluminescence after a short laser pulse (<15 ns) with a wavelength of $\lambda =$ 355 nm (Nd:YAG). Stern-Volmer plots were measured from deoxygenated DMF solutions of the model systems and their components (see Table 1). Elemental analysis was performed in the microanalytical laboratory at the Technische Universität München. GC analysis was performed by using a Varian 490 gas chromatograph equipped with a 1 m COX column and a GC thermal conductivity detector. He (5.0) was used as the carrier gas. Irradiation experiments were performed in a 160 mL Schlenk tube (internal diameter=3 cm) with an LED light source emitting at $\lambda\!=\!(520\pm50)~\text{nm}$ (for details, see the Supporting Information). Reaction vessels were wrapped in black foil prior to sample preparation and unwrapped just before irradiation experiments. DMF solutions containing the catalytic mixture (0.03 mм, i.e., 0.03 mм Ru["] and 0.06 mм Re['] moieties), BNAH (0.1 μ), and TEOA (1.7 μ) were saturated with CO₂ by bubbling for at least 15 min, sealed with a septum, and the pressure was adjusted to 140 kPa. Irradiation experiments were performed in a dark room. For GC analysis, irradiation was suspended to draw 100 μ L samples from the headspace above the solution and inject them directly into the micro gas chromatograph. Irradiation was continued after each GC sampling. TONs were determined from the point at which catalyst activity declined fully, if not stated otherwise, and were defined as $TON = n_{CO}/n_{cat.}$, in which cat. represents the investigated catalytic system or mixture. TOFs were calculated from the linear slope of initial catalytic activity.



Dry solvents were obtained from an MBraun solvent purification system (MP-SPS-800) or dried by using standard methods. NMR solvents were purchased from Sigma–Aldrich and used without further purification. The gases CO₂ (4.5), Ar (4.8), and He (5.0) were purchased from Westfalen. Dmb, pentacarbonylchlororhenium(I), [Ru(cod)Cl₂]_n, 1,2-dibromoethane, NH₄PF₆, DMF, and TEOA were obtained from Sigma–Aldrich or ABCR and used without further purification. BNAH was obtained from TCI. [Re(dmb)(CO)₃CI] (**Re**) was prepared as described recently.^[7]

Syntheses

1,2-bis[4-(4'-methyl-2,2'-bipyridyl)]ethane (dmb-dmb): The product was prepared by following a modified method from Elliott, Freitag, and Blaney.^[20] To a solution of diisopropylamine (1.53 mL, 10.9 mmol, 1.0 equiv.) in THF (25 mL), n-butyllithium (1.6 м in hexanes, 7.0 mL, 11.2 mmol, 1.0 equiv.) was added at -20 °C. After cooling to -78 °C, a solution of dmb (2.05 g, 11.1 mmol, 1.0 equiv.) in THF (40 mL) was added over 25 min. The solution was stirred for 1 h at -78 °C and for another 30 min at -10 °C. After cooling to -78°C again, 1,2-dibromoethane (2.0 mL, 23.2 mmol, 2.1 equiv.) was added. The suspension was warmed to RT and H₂O (50 mL) was added. By addition of NaHCO₃, the pH was adjusted to 8 and the mixture was extracted with diethyl ether (4 \times 50 mL) and dichloromethane (3×50 mL). The organic phases were combined and the solvent evaporated under reduced pressure to yield a white powder. Recrystallization from ethyl acetate afforded colorless crystals of dmb-dmb (1.42 g, 3.87 mmol, 77% yield). ¹H NMR (300 MHz, CDCl₃, 298 K): $\delta = 8.56$ (t, J = 5.3 Hz, 4H), 8.31 (s, 2H), 8.23 (s, 2H), 7.13 (ddd, J=9.4, 5.4, 1.6 Hz, 4H), 3.09 (s, 4H), 2.45 ppm (s, 6H); ^{13}C NMR (75 MHz, CDCl₃, 298 K): $\delta\!=\!156.52$, 155.91, 150.91, 149.32, 149.06, 148.29, 124.87, 123.94, 122.13, 121.23, 36.27, 21.31 ppm; ESI-MS (toluene): *m/z* (%): 367.0 [*M*+H]⁺, 389.0 [*M*+Na]⁺.

[Ru(dmb)₂Cl₂]: The product was prepared by following a modified method from Rau et al.^[12] $[Ru(cod)Cl_2]_n$ (152.0 mg, 0.54 mmol, 1.0 equiv.), dmb (199.3 mg, 1.08 mmol, 2.0 equiv.), and LiCl (192.1 mg, 4.53 mmol, 8.4 equiv.) were suspended in dry DMF (30 mL) and heated in a closed vessel setup in a microwave reactor (125 °C, 50 W, dynamic mode, 2 h). After cooling to 50 °C, the solvent was removed under reduced pressure. The residual solid was suspended in H₂O (500 mL), filtered over a fine frit, and washed with a mixture of H₂O and acetonitrile (9:1, 100 mL). The crude product was eluted from the frit with chloroform (500 mL) and the solvent removed under reduced pressure. Recrystallization from acetonitrile (5 mL) afforded a purple to black powder (112 mg, 20.7 mmol, 38% yield). ¹H NMR (300 MHz, CD₃CN, 298 K): $\delta = 9.83$ (d, J=5.8 Hz, 2 H), 8.21 (s, 2 H), 8.06 (s, 2 H), 7.48 (d, J=5.6 Hz, 2 H), 7.40 (d, J=6.0 Hz, 2 H), 6.82 (d, J=5.1 Hz, 2 H), 2.62 (s, 6 H), 2.40 ppm (s, 6 H); UV/Vis (DMF): λ_{max} (ϵ 10³ m⁻¹ cm⁻¹) = 381 (4.4), 567 nm (4.1); ESI-MS (CH₃CN): *m/z* (%): 505.2 [*M*-Cl]⁺, 540.1 [*M*]⁺, 563.1 [*M*+Na]⁺.

[Ru(dmb)₃](PF₆)₂ (**Ru**): The product was prepared by following a method similar to that of the synthesis of [Ru(R–bpy)₂(L–L)]²⁺ derivatives described by Rau et al.^[12] [Ru(cod)Cl₂]_n (50.0 mg, 0.18 mmol, 1.0 equiv.) and dmb (98.64 mg, 0.54 mmol, 3.0 equiv.) were suspended in dry DMF (30 mL) and heated in a closed vessel setup in a microwave reactor (125 °C, 50 W, dynamic mode, 2 h). The reaction mixture was transferred to a flask, H₂O (30 mL) added, and the solution stirred in an oil bath at 100 °C overnight. After cooling to RT, the solvent was evaporated under reduced pressure and the residual solid dissolved in H₂O (20 mL). A solution of NH₄PF₆ (750 mg, 4.6 mmol, 25.5 equiv.) in H₂O (20 mL) was added and the precipitate collected by filtration over a fine frit. After washing with H₂O (2×25 mL) and diethyl ether (3×25 mL), the solid was dried under vacuum to yield a red powder (144 mg, 0.15 mmol, 86% yield). ¹H NMR (300 MHz, CD₃CN, 298 K): δ = 8.32 (s, 6H), 7.51 (d, *J*=5.8 Hz, 6H), 7.20 (d, *J*=5.8 Hz, 6H), 2.51 ppm (s, 18H); UV/Vis (DMF): λ_{max} (ϵ 10³ m⁻¹ cm⁻¹)=290 (186.0), 462 nm (32.5); ESI-MS (CH₃CN): *m/z* (%): 327.3 [*M*-2 PF₆]²⁺; elemental analysis calcd (%) for C₃₆H₃₆F₁₂N₆P₂Ru·1H₂O (961.72 gmol⁻¹): C 44.96, H 3.98, N 8.74; found: C 44.80, H 3.96, N 8.79.

[Re(CO)₃Cl(dmb–dmb)]: The product was prepared by following a slightly modified method from Wallendael et al.^[13] A solution of [Re(CO)₅Cl] (300 mg, 0.83 mmol, 1.0 equiv.) in MeOH (abs., 300 mL) was added dropwise to a refluxing solution of dmb-dmb (1.06 g, 2.89 mmol, 3.4 equiv.) in toluene (abs., 850 mL) over 4 h. The solution was refluxed for another 4 h, cooled to RT, and the solvent subsequently removed under reduced pressure. The residue was extracted with acetonitrile (3×35 mL) and the solvent removed under reduced pressure. The resulting solid was dissolved in chloroform (25 mL) and the solution filtered and transferred to a flask containing hexane (300 mL). The yellow precipitate was collected by filtration and washed with diethyl ether (6×5 mL). After drying under reduced pressure, a yellow powder (353 mg, 0.53 mmol, 63% yield) was yielded. ¹H NMR (300 MHz, CDCl₃, 298 K): $\delta = 8.88$ (dd, J = 15.0, 5.6 Hz, 2 H), 8.57 (ddd, J = 20.6, 5.0, 0.8 Hz, 2 H), 8.30 (d, J=19.8 Hz, 2 H), 7.96 (d, J=13.5 Hz, 2 H), 7.33 (ddd, J=7.2, 5.5, 1.3 Hz, 2H), 7.17 (ddd, J=5.0, 1.7, 0.8 Hz, 1H), 7.14 (dd, J=5.0, 1.8 Hz, 1 H), 3.22-3.03 (m, 4 H), 2.52 (s, 3 H), 2.45 ppm (s, 3 H); IR (CO): $\tilde{\nu} = 2015$, 1877 cm⁻¹; ESI-MS (CH₃CN): m/z(%): 636.8 [*M*-Cl]⁺, 672.8 [*M*+H]⁺, 694.8 [*M*+Na]⁺; elemental analysis calcd (%) for C₂₇H₂₂ClN₄O₃Re (672.15 g mol⁻¹): C 48.25, H 3.30, N 8.34; found: C 48.33, H 3.47, N 8.14.

[Re(CO)₃Cl(dmb–dmb)Re(CO)₃Cl] (**Re**–**Re**): [Re(CO)₅Cl] (335.8 mg, 0.93 mmol, 2.0 equiv.) and dmb–dmb (170.1 mg, 0.46 mmol, 1.0 equiv.) were suspended in toluene (abs., 10 mL) and refluxed for 5 h. After cooling to RT, the yellow solid formed was filtered off and washed with toluene (1×10 mL) and diethyl ether (2×20 mL). Drying under reduced pressure afforded a yellow powder (447 mg, 0.46 mmol, 98% yield). ¹H NMR (300 MHz, [D₆]acetone, 298 K): δ = 8.98 (d, *J*=5.8 Hz, 2H), 8.91 (d, *J*=5.6 Hz, 2H), 8.63 (s, 2H), 8.46 (s, 2H), 7.72 (dd, *J*=5.8, 1.7 Hz, 2H), 7.60 (d, *J*=5.8 Hz, 2H), 3.44 (s, 4H), 2.59 ppm (s, 6H); IR (CO): $\tilde{\nu}$ =2022, 1920, 1884 cm⁻¹; UV/Vis (DMF): λ_{max} (ε 10³ m⁻¹ cm⁻¹)=292 (67.5), 367 nm (16.4); ESI-MS (CH₃CN): *m/z* (%): 943.4 [*M*–Cl]⁺; elemental analysis calcd (%) for C₃₀H₂₂Cl₂N₄O₆Re₂ (977.84 g mol⁻¹): C 36.85, H 2.27, N 5.73; found: C 36.57, H 2.30, N 5.53.

 $[Re(CO)_{3}Cl(dmb-dmb)Ru(dmb)_{2}](PF_{6})_{2}$ (Re-Ru): [Ru(dmb)₂Cl₂] (56.3 mg, 0.10 mmol, 1.0 equiv.) and [Re(CO)₃Cl(dmb–dmb)] (70.0 mg, 0.10 mmol, 1.0 equiv.) were dissolved in MeOH (abs., 15 mL) and heated to 60°C for 40 h. After cooling to 0°C, aqueous NH₄PF₆ (0.15 м, 18.5 mL, 2.8 mmol, 28 equiv.) was added and an orange to red precipitate formed, which was collected by centrifugation. The precipitate was resuspended in a mixture of H₂O and EtOH (25:1, 25 mL), centrifuged, and collected again. This procedure was repeated 3 times. Then, the residue was dissolved in acetonitrile (2 mL), precipitated in H_2O (40 mL), and collected by centrifugation. This procedure was repeated 3 times. After this, the precipitate was dissolved in acetonitrile (2 mL) and precipitated in diethyl ether (40 mL). Decantation and subsequent drying under reduced pressure afforded an orange to red powder (54.8 mg,



0.04 mmol, 38 % yield). ¹H NMR (300 MHz, CD₃CN, 298 K): δ = 8.90-8.74 (m, 2H), 8.40-8.19 (m, 8H), 7.60-7.04 (m, 14H), 3.23 (s, 4H), 2.61-2.41 ppm (m, 18H); IR (CO): $\tilde{\nu}$ = 2017, 1884 cm⁻¹; UV/Vis (DMF): λ_{max} (ϵ 10³ M⁻¹ cm⁻¹) = 289 (224.1), 461 nm (34.4); ESI-MS (CH₃CN/H₂O): *m/z* (%): 418.3 [*M*-2 PF₆[Re(CO)₃CI]]²⁺, 571.3 [*M*-2 PF₆]²⁺, 1287.3 [*M*-PF₆]⁺; elemental analysis calcd (%) for C₅₁H₄₆CIF₁₂N₈O₃P₂ReRu·2H₂O (1467.65 g mol⁻¹): C 41.74, H 3.43, N 7.63; found: C 41.62, H 3.30, N 7.54.

[Re(CO)₃Cl(dmb–dmb)RuCl₂(dmb–dmb)Re(CO)₃Cl] (**Re**–RuCl₂–**Re**): [Ru(cod)Cl₂]_n (41.7 mg, 0.15 mmol, 1.0 equiv.) and [Re(CO)₃Cl(dmb– dmb)] (200.0 mg, 0.30 mmol, 2.0 equiv.) were suspended in dry DMF (30 mL) and heated in a closed vessel setup in a microwave reactor (125 °C, 50 W, dynamic mode, 2 h). After cooling to 50 °C, the solvent was removed under reduced pressure. The residue was washed with diethyl ether (3×30 mL) and dried under reduced pressure to yield a purple powder (223 mg, 0.15 mmol, 99% yield). IR (CO): $\tilde{\nu}$ = 2016, 1877 cm⁻¹; UV/Vis (CH₃CN): λ_{max} (ε 10³ M⁻¹ cm⁻¹) = 371 (17.0), 567 nm (7.9); ESI-MS (CH₃CN): *m/z* (%): 1480.6 [*M*–Cl]⁺, 1517.3 [*M*+H]⁺; elemental analysis calcd (%) for C₅₄H₄₄Cl₄N₈O₆Re₂Ru (1516.27 g mol⁻¹): C 42.77, H 2.92, N 7.39; found: C 42.56, H 3.14, N 7.18.

[Re(CO)₃Cl(dmb–dmb)Ru(dmb)(dmb–dmb)Re(CO)₃Cl](PF₆)₂

(Re-Ru-Re): Re-RuCl₂-Re (160 mg, 0.11 mmol, 1.0 equiv.) and dmb (194 mg, 1.06 mmol, 10.0 equiv.) were dissolved in a mixture of MeOH (abs., 60 mL) and DMF (abs., 60 mL). The solution was heated to 65 °C under exclusion of light and air for 3 d. After evaporation of the solvent under reduced pressure, the resulting orange solid was extracted with acetonitrile $(1 \times 5 \text{ mL}, 2 \times 2 \text{ mL})$. The solution was passed through a syringe filter and dropped into a flask containing toluene (200 mL). Cooling the solution to 0°C for 1 h afforded an orange precipitate, which was collected by filtration over a fine frit, washed with toluene (3×5 mL), and rinsed from the frit with acetonitrile. The solvent was evaporated under reduced pressure and the orange solid (153 mg, 0.09 mmol) dissolved in EtOH (abs., 90 mL). A solution of NH₄PF₆ (300 mg, 1.84 mmol, 17.4 equiv.) in EtOH (50 mL) was prepared. Both solutions were filtered and subsequently mixed together. After cooling to 0°C for 1 h, the precipitate was collected by filtration over a fine frit and eluted from the frit with acetonitrile (100 mL). H_2O (120 mL) was added, which caused slight precipitation of the complex, and subsequently acetonitrile was added until a clear orange solution remained. The solvent was evaporated under reduced pressure until a cloudy orange precipitate was forming and the rest of the solvent lost most of its color. The precipitate was collected by centrifugation, decantation, and subsequent dilution in acetonitrile to recover the complex from the centrifugation tube. Evaporation of the solvent under reduced pressure and drying under vacuum afforded an orange powder (110 mg, 0.06 mmol, 54% yield). ¹H NMR (300 MHz, CD₃CN, 298 K): $\delta = 8.95 - 8.71$ (m, 4H), 8.53-8.15 (m, 10H), 7.70-6.99 (m, 16H), 3.39-3.03 (m, 8H), 2.69–2.38 ppm (m, 18H); IR (CO): $\tilde{v} = 2017$, 1880 cm⁻¹; UV/Vis (DMF): λ_{max} ($\epsilon \ 10^3 \, \text{m}^{-1} \, \text{cm}^{-1}$) = 290 (232.2), 461 nm (32.5); ESI-MS (CH₃CN/H₂O): m/z (%): 815.4 $[M-2PF_6]^{2+}$; elemental analysis calcd (%) for $C_{66}H_{56}Cl_2F_{12}N_{10}O_6P_2Re_2Ru\cdot 2H_2O$ (1955.56 g mol⁻¹): C 40.54, H 3.09, N 7.16; found: C 40.45, H 2.94, N 7.28.

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