Photochemical CO_2 Reduction with Mononuclear and Dinuclear Rhenium Catalysts Bearing a Pendant Anthracene Chromophore

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Photochemical CO_2 Reduction with Mononuclear and Dinuclear Rhenium Catalysts Bearing a Pendant Anthracene Chromophore

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A series of anthracene-substituted mononuclear and dinuclear rhenium complexes have been studied for photocatalytic CO_2 reduction. The effects on catalytic activity of one *versus* two covalently-linked active sites, their relative proximity to one another, and the pendant organic chromophore are discussed.

Finding a sustainable energy conversion strategy is an urgent scientific and technological challenge given our reliance on non-renewable fossil fuels as a primary energy source coupled with increasing global energy demand.[1] In particular, the development of photocatalysts for CO_2 reduction to carbon-based fuels is attractive for harnessing solar energy with long-term storage in the form of chemical bonds.[2,3] In 1983, Lehn and co-workers reported a single component photocatalyst for CO_2 conversion with general structure $ReX(\alpha\text{-diimine})(CO)_3$ (where X is Cl^- or Br^-).[4] The Re system continues to attract attention as it is a rare example of a complex that plays the role of *both* light absorber and CO_2 reducing catalyst.

We have recently reported the electrocatalytic activity of well-defined dinuclear rhenium catalysts supported by a rigid anthracene-based polypyridyl ligand.[5] A side-by-side investigation of the *cis* and *trans* conformers revealed key differences in mechanism for CO_2 reduction to CO, consistent with single-site and cooperative bimetallic pathways contingent on the relative orientation of metal active sites with respect to the anthracene bridge. In the *cis* conformer ***cis*-Re_2Cl_2**, the rhenium sites are proximal and have an appropriate intermetallic distance for cooperative CO_2 activation and conversion. Indeed, electrocatalytically, ***cis*-Re_2Cl_2** outperformed its *trans* counterpart ***trans*-Re_2Cl_2** with both dinuclear catalysts possessing higher turnover frequencies (TOFs) and comparable Faradaic efficiencies relative to $Re(bpy)(CO)_3Cl$.[5]

For photocatalytic applications, the presence of two metal centers may enable more efficient accumulation of reducing equivalents for improved CO_2 conversion.[6] Dinuclear rhenium catalysts, tethered together by flexible alkyl chains linking two bipyridines, have been reported for photocatalytic CO_2 reduction.[7,8] These catalysts were shown to outperform their mononuclear parent catalyst with greater durability and higher TOFs observed as the alkyl chain was shortened. However, this approach lacks structural integrity and samples indiscrete conformations in solution. Other Re_2 catalysts have not been studied photocatalytically or feature ligand scaffolds that preclude intramolecular bimetallic CO_2 activation and conversion.[9-11] Thus the desirable design parameters surrounding this approach remain poorly understood.

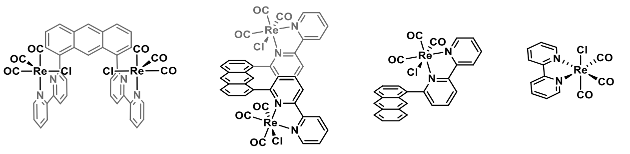
cis-Re_2Cl_2 *trans*-Re_2Cl_2 anthryl-Re $Re(bpy)(CO)_3Cl$

Figure 1. Structures of Re photocatalysts studied for CO_2 reduction.

In general, plausible pathways for accelerated catalysis with a dinuclear complex relative to a mononuclear analogue include: (1) cooperative catalysis in which both metal centers are involved in substrate activation and conversion, or (2) one site acting as an efficient, covalently-linked photosensitizer to the second site performing CO_2 reduction. In the dual active site mechanism (1), an intramolecular pathway may exist involving cooperative binding of the substrate where CO_2 is bridged between rhenium centers, potentially increasing the basicity of CO_2 and the rate of catalysis by facilitating C-O bond cleavage and the elimination of water in subsequent steps. Intramolecular CO_2 binding between metal centers is only expected for ***cis*-Re_2Cl_2** since CO_2 is geometrically inhibited from interacting with both rhenium centers in ***trans*-Re_2Cl_2**.

For the photosensitizer pathway (2), it is generally accepted that $Re(bpy)(CO)_3Cl$ functions through a bimolecular pathway where one complex operates as a photosensitizer (PS) and a second complex operates initially as a photocatalyst for the first reduction, then as an electrocatalyst which receives the second electron needed for the $2e^-$ reduction of CO_2 to CO from a reduced PS in solution.[6] In this

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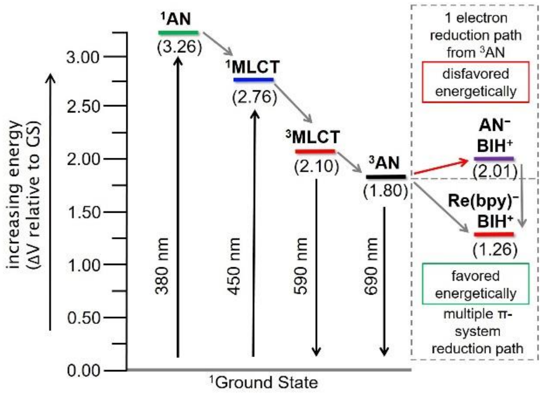
pathway, ***cis*-Re_2Cl_2** and ***trans*-Re_2Cl_2** are predicted to have superior reactivity to mononuclear derivatives since both dinuclear systems could utilize one Re site as a PS and the second as the catalyst, thereby increasing the relative concentration of PS near the active site. This effect would be most dramatic at low concentrations where the intermolecular reaction necessary for the monomers would be slow. Higher durability at low concentrations is known for photocatalyst systems; however, most rely on a high PS loading to keep the effective concentration of PS high in the dilute solution.[12,13] The approach pursued here may enable a high rate of reactivity to be retained at low concentrations while promoting increased durability.

In addition, sufficiently long-lived excited states are required for efficient solar-to-chemical energy conversion, where longer lifetimes result in more efficient excited-state quenching to generate catalytic species. One avenue to more persistent excited states in metal polypyridine complexes is to link them with organic chromophores possessing long-lived triplet excited states where decay pathways are strongly forbidden.[14-19] Anthryl substituents have served effectively as the organic component in a variety of systems.[17-19] Important light absorption and excited-state decay pathways of such systems are depicted in **Scheme 1** where excited states are ultimately funnelled downhill by internal conversion and/or intersystem crossing to the anthracene-based triplet excited state.

Beyond anthracene's potential to act as a triplet excited-state acceptor, a rigid scaffold for promoting cooperative bimetallic reactivity, and its impact on reduced species as a large π-system with extended delocalization, the anthracene moiety also functions as a sterically bulky group that may inhibit deleterious intermolecular catalyst deactivation pathways. Indeed, an iridium-based single-component photocatalyst bearing an anthracene substituent was recently reported for CO_2 reduction with improved stability.[20] In this context, we report the photocatalytic activity and photophysical properties of the dinuclear Re complexes shown in **Figure 1**. For comparison, experiments employing the same set of conditions were also performed in parallel with mononuclear chromophore/catalysts $Re(bpy)(CO)_3Cl$ and **anthryl-Re** to disentangle the effect of more than one metal active site as well as the possible involvement of the pendant organic chromophore in photocatalytic activity (**Figure 1**).

For photosensitizer-free catalysis, the rhenium catalysts are initially photoexcited directly into their long wavelength metal-to-ligand charge transfer (MLCT) absorption. This is followed by reductive quenching in the presence of a sacrificial donor to form a ligand-centered radical anion. With $Re(bpy)(CO)_3Cl$, the ligand-centered anion is delocalized on the bpy ligand prior to Cl^- dissociation.[6,22] In the Re_2Cl_2 complexes, the Re(bpy) units are in weak electronic communication *via* the anthracene backbone (comproportionation constants (K_C) of 50 were determined electrochemically for each conformer),[5] which could facilitate intramolecular electron transfer between active sites.



Scheme 1. Light absorption and excited-state electron transfer pathways in Re compounds with pendant anthracene.[21]

As will be shown below, direct irradiation of the Re complexes in the presence of a sacrificial electron donor leads to CO_2 reduction to CO. While photocatalysis was expected, the nature of the lowest energy excited state is *different* for the catalysts bearing anthracene versus $Re(bpy)(CO)_3Cl$. In deaerated solutions (N_2) all three anthracene containing complexes exhibit luminescence in the yellow/red spectral region as well as structured emission at longer wavelengths (Figure S1). The lifetime of the yellow/red emission is approximately 400 ns for the monometallic **anthryl-Re** complex, and 200 ns for both bimetallic Re complexes. The long wavelength emission (with vibronic components having maxima at 688-700 nm and 764-772 nm) has a double exponential decay with one component being 6-15 μs and the other 23-90 μs (Table S1). This luminescence is completely quenched in the presence of O_2 and, given the energy, lifetime and O_2 quenching behavior, this emission almost certainly arises from an anthracene-localized triplet state obtained following energy transfer from the ^{3}MLCT excited state.[23] This behavior is similar to reported metal polypyridine photo-sensitizers with pendant anthracene (or pyrene) functionality.[17-19]

It is not clear for these systems how the anthracene-localized triplet reacts with the BIH electron donor to generate the reduced Re complex (quenching data is shown in Figure S2). Reduction of the anthracene-localized triplet ($E_0 \sim 1.8$ eV) by BIH to generate the anthracene anion / BIH cation pair is thermodynamically uphill by at least 0.21 V (eq 1, **Scheme 1**).

$$\text{Anthracene} + e^- \leftrightharpoons (\text{Anthracene})^- \quad E_{(AN/AN^-)} = -2.25\text{ V } vs\text{ Fc}^{+/0} \quad (1a)$$

$$^3(\text{Anthracene}) \rightarrow \text{Anthracene} \quad E_g^{opt} \sim 1.8\text{ eV} \quad (1b)$$

$$\text{BIH} \leftrightharpoons \text{BIH}^+ + e^- \quad E_{(BIH+/BIH)} = -0.24\text{ V}^{24} \quad (1c)$$

For the reduced Re/oxidized BIH pair, the energy is 1.26 V above the ground state (**Scheme 1**) and is therefore accessible from the anthracene triplet (at 1.8 eV), but involves electron transfer between the Re complex and the BIH while using the energy of the anthracene triplet. Note that an intramolecular photoredox reaction between the anthracene triplet and the Re center ($E_{(AN+/AN)} \sim 0.8$ V; $E_{(Re(bpy)/Re(bpy-))} \sim -1.5$ V) is also endergonic. Regardless of mechanism, these data clearly indicate that photoexcitation of the three anthryl Re complexes results in an excited state that is largely localized on the anthracene as a triplet. Excited-state electron transfer between this triplet and BIH occurs ($k_q \sim 1\text{-}5 \times 10^7$ $M^{-1}s^{-1}$ for the three complexes) to produce the reduced complex/oxidized BIH pair that, following decomposition of the BIH cation radical, leaves the reduced Re complex to react with CO_2. Transient absorption spectroscopy shows that the 1e⁻ reduced Re complexes formed by BIH photoreduction under Ar or CO_2 atmosphere exhibit no reaction over the first ~1 ms (**Figure 2**). This clearly shows that disproportionation and reaction with CO_2 do not occur on this time scale.

Having found that anthracene plays a significant role in the photochemistry of ***cis*-Re_2Cl_2**, ***trans*-Re_2Cl_2**, and **anthryl-Re**, we turned to photocatalytic CO_2 reduction in the presence of BIH to understand how a dinuclear approach affects catalysis in a rigidified

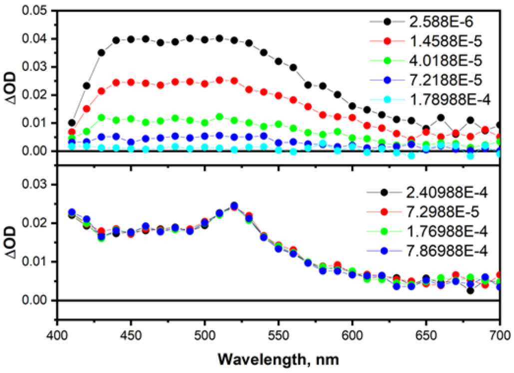


Figure 2. Transient absorption spectra at specified times after pulsed laser excitation (λ_{ex} = 355 nm) of **_trans_-Re$_2$Cl$_2$** in DMF under Ar purge (top) and **_trans_-Re$_2$Cl$_2$** with BIH (0.01 M) under CO$_2$ purge (bottom). No reaction of the one-electron reduced **_trans_-Re$_2$Cl$_2$** complex with CO$_2$ is evident in the first 800 μs following excitation.

framework. Photocatalysis was conducted with a solar simulated spectrum and CO was the only product observed by headspace GC analysis (Figures S5 and S6).

Concentration effects were studied for all catalysts given the mechanistic implications expected of these experiments (**Figure 3**, Table S2). Reported TOFs are for the fastest 20 min time period within the first 40 min as an estimate of the initial rate prior to significant catalyst deactivation. Broadly comparing dinuclear complexes to mononuclear complexes, significantly higher reactivity is observed at low concentrations (0.05 mM) for the dinuclear complexes (158-128 TOF h^{-1}, 105-95 TON) when compared to the mononuclear complexes (43-17 TOF h^{-1}, 34-16 TON). If the total concentration of metal centers is held constant, the mononuclear catalyst concentration at 0.1 mM can be directly compared to the 0.05 mM dinuclear catalyst concentration. This comparison shows a similar difference in the initial rates of mononuclear versus dinuclear catalysts with the mononuclear catalysts showing TOF values of 43-23 h^{-1}. These results suggest a PS-based pathway is present as this explains how **_cis_-Re$_2$Cl$_2$** and **_trans_-Re$_2$Cl$_2$** have comparable reactivity despite their structure, while substantially outperforming the mononuclear complexes at low concentrations where intermolecular collisions are fewer. As the concentration increases, TOF and TON values converge to similar rates and durabilities for all catalysts, presumably due to intermolecular deactivation pathways that are prevalent at high concentrations. Interestingly, all of the anthracene-based catalysts effectively stop evolving CO after the first hour, while Lehn's benchmark catalyst continues CO production up to 2 hours. In contrast to reported systems bearing sterically bulky substituents that showed improved stability by limiting bimolecular deactivation pathways, **anthryl-Re** is found to be less durable (*vide infra*).

Comparing the two dinuclear catalysts, **_trans_-Re$_2$Cl$_2$** has higher TOF and TON values at the lowest concentration analyzed in **Figure 3** (0.05 mM). As the concentration increases, TOF and TON values diminish faster for the *trans* conformer relative to its *cis* counterpart; qualitatively, their values follow similar trajectories. The faster decrease in TOF and TON for the *trans* conformer suggests that it is more susceptible to intermolecular catalyst-catalyst deactivation pathways. The performance trends for the Re$_2$ complexes strongly suggests one rhenium site is acting as a PS while the other performs catalysis. Moreover, these results indicate intramolecular electron transfer between sites is similar for both dinuclear catalysts, consistent with their equivalent K_C values.[5] To ensure the Re$_2$ complexes are not photoisomerizing to the same species in solution, the catalysts were independently irradiated in d_6-DMSO under N$_2$ for up to 8 h. No appreciable interconversion of either isomer was observed by ^{1}H NMR, which suggests both species retain their conformation over the reaction period. At very low concentrations (1 nM) where some photocatalytic systems show higher TON values,[12] the highest performing catalyst **_trans_-Re$_2$Cl$_2$** gives a remarkable 40,000 TON for CO. Notably, CO from 1 nM Re(bpy)(CO)$_3$Cl was undetectable by the GC system used in these studies.

The two mononuclear complexes show TON values at dilute concentrations that are lower than that observed at intermediate concentrations before again decreasing to lower TONs at high concentrations. The TON values for the mononuclear catalysts peak at approximately 0.1-0.2 mM with **anthryl-Re** peaking at a lower concentration than Re(bpy)(CO)$_3$Cl. This behaviour can be rationalized if the reaction is bimolecular as prior reports strongly suggest for these types of systems.[6] At low concentrations, a PS complex and a catalyst complex interact less frequently and potential decomposition of either species is more competitive. At intermediate concentrations, more productive reactions can occur between PS and catalyst complexes. In the high concentration regime, catalyst-catalyst deactivation pathways become competitive with CO production pathways. This highlights a key difference between the mononuclear catalysts and the dinuclear systems which retain a high effective concentration of PS as it is covalently linked to a reactive site at low overall concentration. This circumvents to some degree the non-catalyst-catalyst deactivation mechanisms by maintaining a fast CO production pathway. Comparing TOFs for the monomers, **anthryl-Re** has a ~2-fold faster rate of catalysis at low

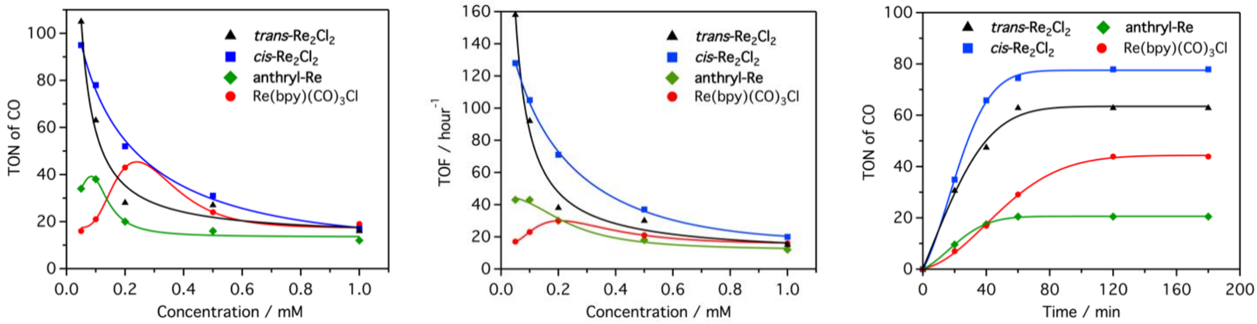


Figure 3. Left) Maximum TON *vs* catalyst concentration. Middle) TOF *vs* catalyst concentration. TOF is the fastest value measured within first two timepoints. Right) TON for CO production *vs* time for 0.1 mM **_cis_-Re$_2$Cl$_2$**, 0.1 mM **_trans_-Re$_2$Cl$_2$**, 0.2 mM **anthryl-Re**, and 0.2 mM Re(bpy)(CO)$_3$Cl. *Conditions*: DMF containing 5% triethylamine, 10 mM BIH; irradiated with a solar simulator (AM 1.5 filter, 100 mW/cm^2).

concentrations. A significantly higher molar absorptivity was measured at 370 nm for **anthryl-Re** (11,100 $M^{-1}cm^{-1}$) relative to $Re(bpy)(CO)_3Cl$ (3,800 $M^{-1}cm^{-1}$) and the excited state lifetime of **anthryl-Re** is significantly longer than for $Re(bpy)(CO)_3Cl$ (> 1 µs *vs* < 100 ns)[24] enabling a greater degree of BIH quenching. These factors may explain the difference in rates at these concentrations (Figure S3, Table S1).

Quantum yield estimations also show a significant difference in the catalytic behaviour of the mononuclear versus dinuclear catalysts (Figure S4, Table S2). Between 0.05 mM and 0.5 mM the dinuclear complexes have estimated quantum yields of 1.6-4.3% with higher concentrations showing higher quantum yields. In the low concentration regimes, the dinuclear catalysts have roughly double the quantum yield of the mononuclear catalysts. This offers additional evidence that pathway 2 is operable in that both dinuclear complexes have relatively high quantum yields at low concentrations. At the highest concentration evaluated (1.0 mM) where the mononuclear catalyst can operate through an intermolecular PS pathway most efficiently, $Re(bpy)(CO)_3Cl$ and the dinuclear catalysts have similar quantum yields (4.4-4.6%). Based on previous work[6,22] and the results described here, a proposed mechanism for the Re_2 photocatalysts is shown in **Figure 4**, which illustrates a division of duties for the two active sites and allows access to an exceptional TON value for carbon monoxide of 40,000.

Two dinuclear Re catalysts with well-defined, shape persistent structures and a mononuclear analogue have been studied for light-driven CO_2 reduction. Their photocatalytic properties have been explored in parallel with benchmark catalyst, $Re(bpy)(CO)_3Cl$. Incorporation of a pendant anthracene group on the bipyridyl ligand (**anthryl-Re**) had a modest effect on the catalytic performance. In contrast, the Re_2 catalysts perform significantly better (~4X higher TON) than the benchmark system when the relative concentration in rhenium is held constant (0.1 mM dinuclear *vs* 0.2 mM mononuclear). Despite the structural differences of ***cis*-Re_2Cl_2** and ***trans*-Re_2Cl_2**, their initial rates are comparable with both being dramatically faster (~6X higher) than the mononuclear complexes, which have comparable rates to each other. This suggests that the mechanism for CO_2 reduction may be similar for the two dinuclear complexes and does not require a specific spatial orientation of the Re active sites. The excited-state kinetics and emission spectra reveal that the anthracene backbone plays a more significant role beyond a simple structural unit. Evidence of an anthracene triplet state is observed, and given the unlikely event of direct reduction of the anthracene triplet state by sacrificial reductant BIH, a more complex mechanism is likely taking place beyond the Re(bpy) excitation/BIH reduction kinetics.

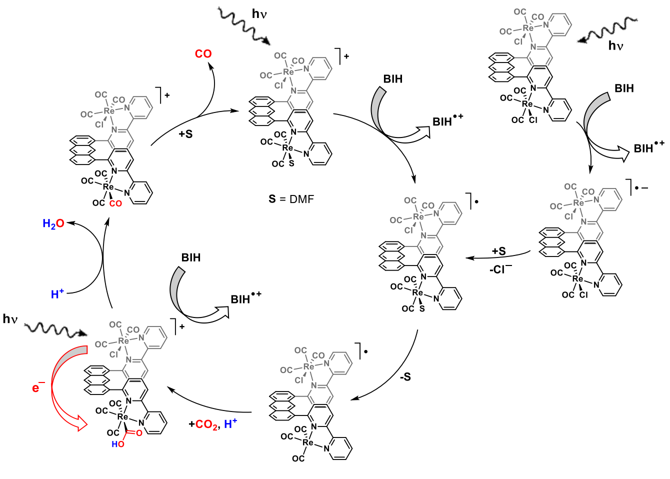


Figure 4. Proposed catalytic cycle for photochemical CO_2 reduction to CO with the dinuclear Re catalysts, ***cis*-Re_2Cl_2** or ***trans*-Re_2Cl_2**. The *trans* conformer is shown in the specific example above.

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Conflicts of interest

The authors declare no competing financial interest.

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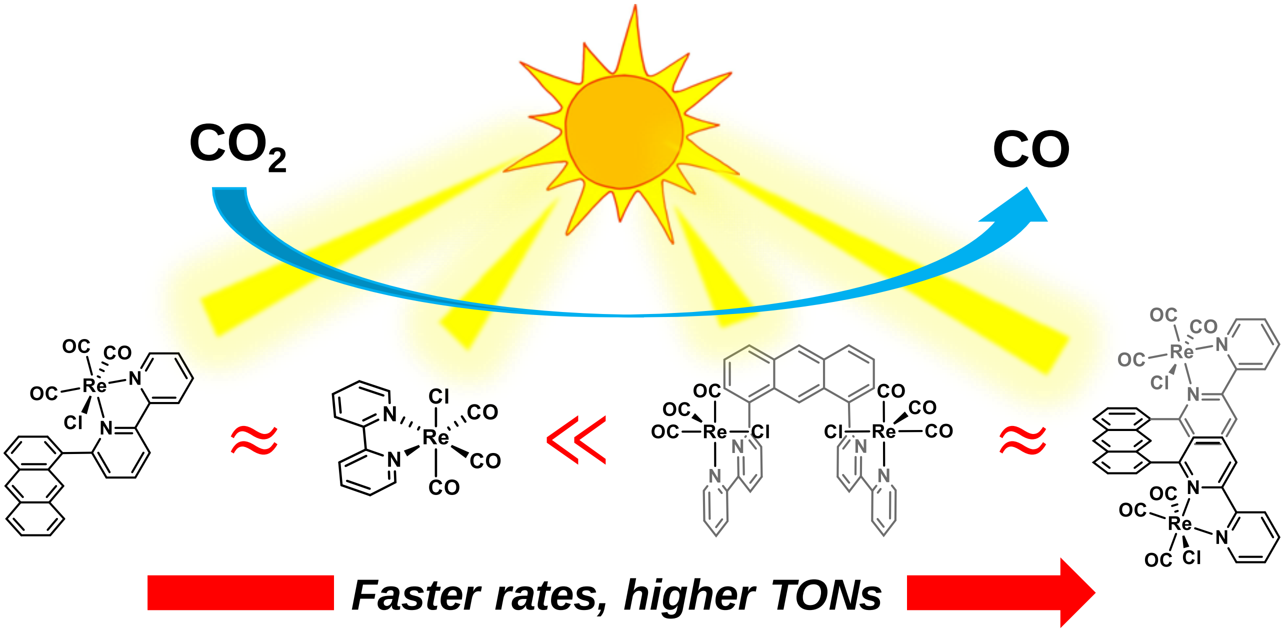
TOC Graphical Abstract



Well-defined dinuclear rhenium photocatalysts featuring an anthracene chromophore are significantly faster and more durable than their mononuclear counterparts.