Photochemical and Electrochemical Reduction of Carbon Dioxide Catalyzed by a Polyoxometalate-Organic Photosensitizer Complex

Chandan Dey,[a] and Ronny Neumann*[a]

Abstract: A manganese substituted Anderson type polyoxometalate, $[MnMo_6O_{24}]^{9-}$, tethered with an anthracene photosensitizer was prepared and used as catalyst for CO_2 reduction. The polyoxometalate-photosensitizer hybrid complex, obtained by covalent attachment of the sensitizer to only one face of the planar polyoxometalate, was characterized by NMR, IR and mass spectroscopy. Cyclic voltammetry measurements show a catalytic response for the reduction of carbon dioxide, thereby suggesting catalysis at the manganese site on the open face of the polyoxometalate. Controlled potentiometric electrolysis showed the reduction of CO_2 to CO with a TOF of ~15 sec^{-1}. Further photochemical reactions showed that the polyoxometalate-anthracene hybrid complex was active for the reduction of CO_2 to yield formic acid and/or CO in varying amounts dependent on the reducing agent used. Control experiments showed that the attachment of the photosensitizer to $[MnMo_6O_{24}]^{9-}$ is necessary for photocatalysis.

Introduction

The reduction of the carbon dioxide footprint is an important goal in our generation towards a more sustainable society. One objective could be the reduction of CO_2 to fuels, thereby leading to a "carbon neutral" fuel regime. Both photochemical and electrochemical approaches are being investigated.[1] Photocatalytic CO_2 reduction typically involves a photosensitizer (PS), an electron/proton donor, often a trialkyl amine and a catalyst. An one-electron reduced photosensitizer (PS*$^-$) is formed by excitation of the photosensitizer with light and subsequent quenching of photo-excited state (PS*) by an electron donor.[2] Placing the catalyst and photosensitizer in close proximity abets the electron transfer process that occurs either through space or through chemical bonds.[3] In this context, already in 1992, it was reported that a binuclear complex, Ru-(phen)$_2$(phen-cyclam-Ni)(ClO$_4$)$_4$·2H$_2$O complex showed improved photocatalytic activity for CO_2 reduction in comparison to a mixture of the photosensitizer, Ru(phen)$_3^{2+}$, and Ni(cyclam)$^{2+}$, the catalyst where cyclam = 1,4,8,11-tetraazacyclotetradecane, and phen = 1,10-phenanthroline].[4] More recently, Ishitani and co-workers showed that [Ru{bpyC$_3$bpyRe(CO)$_3$Cl}$_3$]$^{2+}$, a tetranuclear complex and [(dmb)$_2$Ru(bpyC$_3$bpy)Re-(CO)$_3$Cl]$^{2+}$, a binuclear complex are better photocatalysts for the reduction of CO_2 to CO

than a mixture of mononuclear complexes of same ratio [bpyC$_3$bpy = 1,3-bis(4'-methyl-[2,2']bipyridinyl-4-yl)propan-2-ol and dmb = 4,4'-dimethyl-2,2'-bipyridine].[5] In a further report, it was observed that the complex with shortest chain length is best catalyst in a series of binuclear complexes, [{Ru(dmb)$_2$}-LL-{Re(CO)$_3$Cl}]$^{2+}$, where the bridging unit was systematically varied between LL = 1,2-bis(4'-methyl-[2,2']bipyridinyl-4-yl)-ethane/ butane/ hexane].[6]

Polyoxometalates are metal-oxide clusters only rarely studied as catalysts for CO_2 reduction.[7] Previously, a Ru(III) substituted Keggin type polyoxometalate, [(C$_6$H$_{13}$)$_4$N]$_5$[Ru^{III}(H$_2$O)SiW$_{11}$O$_{39}$] was studied as a photocatalyst for reduction of CO_2 to CO.[8] A similar cobalt(II) substituted compound, [(C$_8$H$_{17}$)$_4$N]$_6$[Co(II)SiW$_{11}$O$_{39}$] was studied as an electrocatalyst.[9] Additionally, phosphotungstic acid has been used as an electron "shuttle" when attached to a rhenium catalysts active for reduction of CO_2 to CO, thereby allowing either the use of H$_2$ as the electron/proton donor instead of tertiary amines,[10] or photoelectrochemical CO_2 reduction with visible light and low negative potentials.[11] The experiments and calculations show that excitation of the intra-valence charge transfer band of the reduced polyoxometalate,[11,12] in effect the photosensitizer, lead to electron transfer to the attached catalyst allowing CO_2 reduction. All of the research described above involves the use of type I polyoxometalates, those where the tungsten/molybdenum addenda have one terminal oxo ligand. During the catalytic cycle a reversible reduction of the non-bonding HOMO orbital of the polyoxometalate is possible. Type II polyoxometalates, with two terminal oxo ligands, have an anti-bonding HOMO orbital and the addenda atoms are not reduced. Such polyoxometalates are much less investigated in the context of catalysis and there have been no reports on their use for the photoreduction of CO_2.

The functionalization of polyoxometalates with organic/metalorganic tethers by various methods is a broad topic.[13] Related to this article, Keggin and Dawson type I polyoxometalates have been covalently functionalized with both ruthenium and iridium photosensitizers.[14] Also the functionalization of Anderson type II polyoxometalates,[15] invariably involves the attachment of N-functionalized tris(hydroxymethyl)aminomethane derivatives to both faces of the polyoxometalate.[16] This strategy was used to attach two 2,2'-bipyridine-iridium photosensitizers to an Anderson polyoxometalate allowing a visible light driven hydrogen evolution reaction from water where it was reported that the photosensitizer bound catalyst was more efficient than a simple mixture of polyoxometalate and photosensitizer.[17] There is one report on non-symmetrically functionalized Anderson derivatives, that is those with two different functional groups on each face,[16c] but the selective substitution on only one face of an Anderson polyoxometalate remains a challenge.[18] Studies on mechanism

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of photocatalytic CO_2 reduction suggest that the intermediate ligation of CO_2 to the metal centre of reduction catalyst.[19] Therefore, the objective of this research was to use the planar Anderson type II polyoxometalate $[Mn^{III}Mo_6O_{24}]^{9-}$, as a catalyst for CO_2 reduction, where the substituted metal, Mn(III), can be reduced in preference to the Mo addenda atoms. Attachment of a photosensitizer to *only* one face of $[Mn^{III}Mo_6O_{24}]^{9-}$, yields a hybrid complex as an electro- and photo-catalyst where there is an accessible site for coordination of CO_2 as shown in Scheme 1.
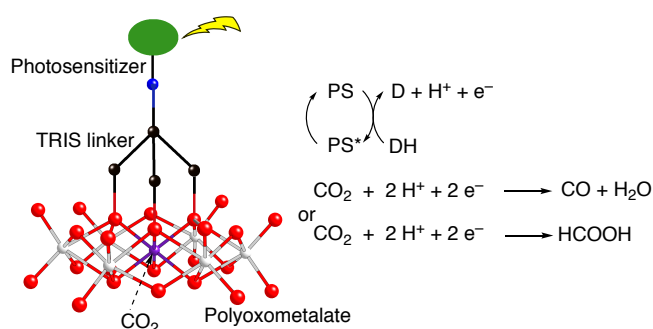
Scheme 1. The Polyoxometalate-Photosensitizer (Anthracene) Hybrid Complex (Not Drawn to Scale) for the Reduction of CO_2 and the Reactions Involved. N-Blue, C-Black, O-Red, Mo-Silver, Mn-Magenta.

Results and Discussion

Synthesis. The synthetic pathway for the preparation of the polyoxometalate-anthracene complex is shown in Scheme 2. Thus, anthracene-9-carbaldehyde (1) was reacted with tris(hydroxymethyl)aminomethane (TRIS) to form the imine (2), which was then reduced to yield the respective amine (3). This tripodal precursor was reacted with the octamolybdate, $Q_4[\alpha-Mo_8O_{26}]$ (Q = tetra-n-butylammonium and $Mn(OAc)_3$ in a 1:1:1 ratio, to yield the polyoxometalate-anthracene hybrid complex (4) substituted on one face of the polyoxometalate. The easier substitution of anthracene on both faces to yield (5) was also carried out for comparison (see ESI).
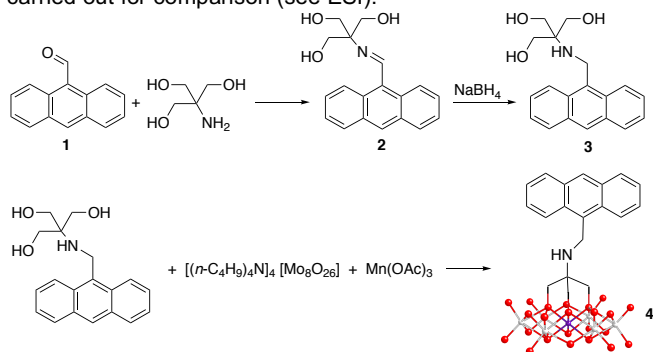
Scheme 2. Pathway for the Synthesis of the Polyoxometalate-Anthracene Hybrid Complex

Compound 4 was characterized by ^1H NMR, which showed the expected peaks for the arene and the quaternary ammonium

hydrogen atoms and the unique strongly deshielded peak, observed downfield at ~62 ppm, associated with the tripodal CH_2 moiety in the proximity of the paramagnetic Mn(III) heteroatom of the polyoxometalate. The evidence, however for the formation of the desired hybrid complex, 4, comes from ESI-MS measurements, as presented in Figure 2. For comparison, the spectrum for the 1:2 polyoxometalate-anthracene complex is shown in the SI, Figure S1, where clearly different high molecular weight peaks are observed.
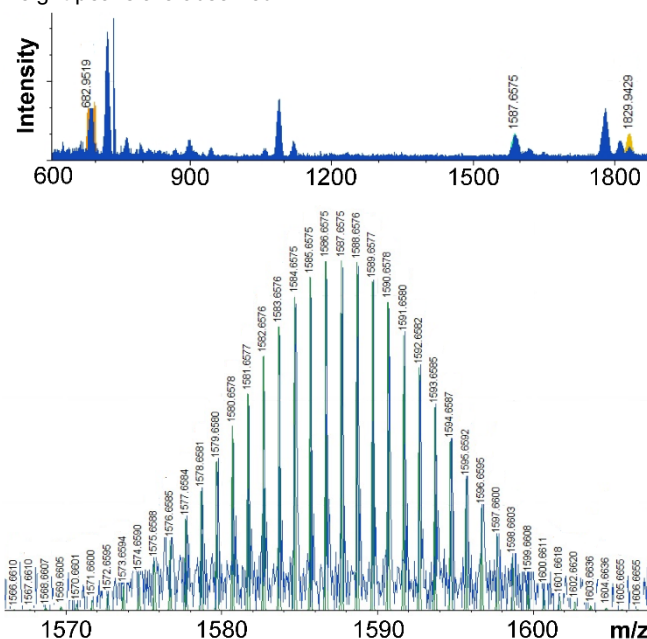

Figure 1. Negative ion HR-ESI-MS of **4**. The full spectrum (top) has three clearly identifiable peaks at 1829.9429 for $[MnMo_6O_{24}][C_{19}H_{18}N][Q_2][Na_3]^{1-}$; 1587.6575 for $[MnMo_6O_{24}][C_{19}H_{18}N][Q][Na_3][H]^{1-}$ and 689.9513 for $[Mo_3O_{10}][Q]^{1-}$. On the bottom, the isotope pattern of the peak at 1587.6575 is presented (experimental in blue; simulated using mMass in green).
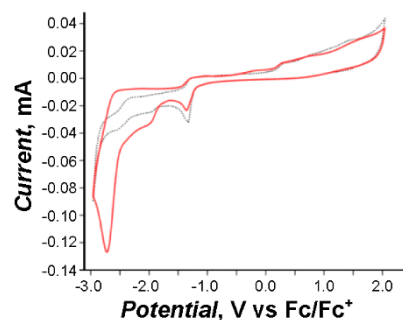

Figure 2. Cyclic voltammograms of 4 under 1 bar Ar (black dotted line) and under 1 bar CO_2 (red line). Cathode, anode and reference electrode were glassy carbon, Pt wire within a glass frit and a calomel electrode respectively. Scan rate - 50 mV/s. The system was calibrated with Fc/Fc+.

Electrocatalysis. The cyclic voltammetry of 1.1 mM **4** was carried out in acetonitrile using 0.1 M tetrabutyl ammonium perchlorate as the supporting electrolyte. Glassy carbon and Pt wire fitted within a glass frit were used as the working and counter electrode respectively. Calomel was used as reference electrode. However, values in the plot was calibrated vs Fc/Fc+. Under Ar the

CV shows a reduction peak at -1.32 V associated with Mn^{3+}/Mn^{2+} redox couple. Three additional reduction peaks at -1.37 V, -1.96 V and -2.51 V were considered as reductive electron transfer to aromatic rings and/or further reduction of the Mn atom. Under 1 bar CO_2 atmosphere a catalytic wave for CO_2 reduction is clearly evident at 2.7 V vs Fc/Fc$^+$, Figure 2. Only a very weak catalytic wave was observed for the disubstituted polyoxometalate where there was no Mn – CO_2 binding site (Figure S5 in SI). Constant potential electrolysis was carried out at -2.65 V (vs Fc/Fc+) using 5 μmol **4** in 5 mL acetonitrile with 0.1 M tetrabutyl ammonium perchlorate as electrolyte, a glassy carbon disk of a 0.3 cm diameter as the cathode and a Pt wire anode. After 22 h, 1.12 μmol CO was obtained with no other detectable products by GC-TCD of the gas phase and NMR of the solution. Considering that **4** has an average diameter of about 2 nm, the maximum surface coverage of **4** on the glassy carbon electrode is around 1 picomole. Therefore, the turnover frequency for the electrocatalytic formation of CO is around 10-20 sec^{-1}.

Photocatalysis. The UV-vis absorption of the $[MnMo_6O_{24}]$ anion itself was extrapolated from the Anderson polyoxometalate substituted on both faces with TRIS (compound **6**). As shown in Figure S2 there is no appreciable absorption in the visible region. On the other hand, **4** does have absorption maxima at λ_{max}= 365 nm (ε = 455 M^{-1} cm^{-1}) and 385 nm (ε = 410 M^{-1} cm^{-1}) and with an onset of the absorption well into the NIR region, Figure S3. Photocatalytic reduction of CO_2 was carried out by irradiation with ten 8 W warm white fluorescent tubes in acetonitrile using trimethylamine as the electron/proton donor. Thus, in a Young NMR tube a 200-fold excess of trimethylamine was added to 0.5 mL of 3.8 mM solution of **4** in acetonitrile, which was irradiated under 1 bar $^{13}CO_2$ for 17 h at room temperature. Only formic acid was formed as the reduction product. The turnover number, estimated by ^{13}C NMR was about 2-3. ^1H NMR measurements of the reaction mixture showed that the peak at 62 ppm remained unchanged indicating that **4** was stable. A control experiment without CO_2 to support the stability of **4** showed no product formation and the recovery of **4**. Interestingly, an identical experiment replacing trimethylamine with a 25-fold excess of 1-benzyl-1,4 dihydronicotinamide as electron/proton donor yielded ^{13}CO as the sole product; no formic acid was detected. One should note that triethanolamine decomposes **4** because of transesterification releasing **3**. A mixture of **6** and anthracene showed no product formation.

Conclusions

An Anderson polyoxometalate anion, $[MnMo_6O_{24}]^{9-}$, has been successfully synthesized with an active photosensitizer (anthracene) tethered to only one face of the anion. This leads to an available Mn catalytic site for the reduction of CO_2. Both electrocatalytic and photocatalytic reduction to CO or HCOOH only was observable using this new catalyst based on earth abundant elements.

Experimental Section

Synthesis of the polyoxometalate-anthracene hybrid complex, **4**. TRIS (2 mmol) and of 9-anthracenaldehyde (2 mmol) were stirred in 10 mL dry methanol for 36 h. After removal of the solvent, the imine product, **2**, was filtered and washed with water and dried under vacuum. ^1H NMR in DMSO-d$_6$: δ - 3.79 (6H), 4.67 (3H), 7.52 (4H), 8.08 (2H), 8.49 (2H), 8.62

(1H), 9.42 (1H). ESI-MS m/z: **2** - 309.4; **2** + Na - 332.4; 2 x **2** + Na - 641.8. Compound **2** (0.1 mmol) was reacted with NaBH$_4$ (1.3 mmol) in 15 mL methanol for 2 days. After removal of the solvent, the amine product, **3**, was filtered and washed with water and dried under vacuum. ^1H NMR in DMSO-d$_6$: δ - 3.58 (6H), 4.50 (3H), 4.70 (2H), 7.50 (4H), 8.04 (2H), 8.46 (1H), 8.50 (2H). ESI-MS m/z: **3** + H - 312.28; **3** + Na - 334.27. $Q_4[\alpha-Mo_8O_{26}]$ (270 mg, 0.13 mmol) prepared according to the literature reported method,[20] $Mn(OAc)_3\cdot2H_2O$ (35 mg, 0.13 mmol), and **3** (40 mg, 0.13 mmol) were reacted in 5 mL dry acetonitrile at 80 °C for 25 h. After the reaction the undissolved materials were separated from the mixture by centrifugation. The upper orange-yellow solution was collected and solution diethyl ether was diffused into the solution. The pale orange colored product, $Q_6[MnMo_6O_{24}](C_{19}H_{18}N)$, **4** precipitated. It was separated by filtration and dried. The ^1H NMR in CD$_3$CN showed significantly broadened peaks at: δ - 0.97, 1.37, 1,61 and 3.11 ppm attributed to the tetrabutyl ammonium cation; δ - 5.55 and 6.18 ppm attributed to the benzylic CH$_2$ and the NH moieties; δ - 7.65, 8.11 and 8.48 ppm attributed to the anthracene moiety; δ - 61.90 ppm for the CH$_2$ adjacent to the polyoxometalate anion. IR, (KBr pellet, cm-1): 2961, 2871, 1635, 1574, 1480, 1380, 1153, 1127, 1038, 939, 920, 901, 800, 737, 667, 564.

Electrochemistry: Cyclic voltammetry measurement were carried out in acetonitrile using 0.1 M tetrabutyl ammonium perchlorate as the supporting electrolyte. Glassy carbon and Pt wire fitted within a glass frit were used as working and counter electrode respectively. Calomel was used as reference electrode. The scan rate was 50 mV/s. The cyclic voltammograms were plotted with respect to Fc/Fc$^+$ measured separately. Constant potential electrolysis as carried out using a glassy carbon cathode and Pt wire anode fitted within a glass frit at -2.65 V.

Photochemistry: Photocatalytic reduction of CO_2 was carried out by irradiation with ten 8 W warm white fluorescent tubes (Walter T5 8W 220V 400lm DL) in acetonitrile within an enclosed chamber.

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COMMUNICATION

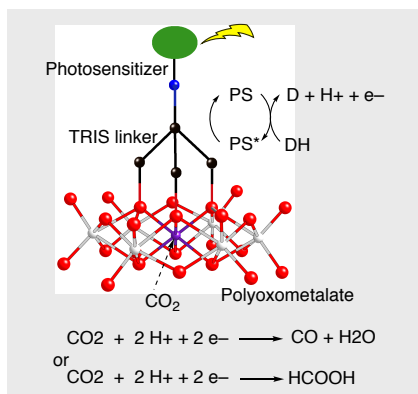**Entry for the Table of Contents** (Please choose one layout)

Layout 1:

COMMUNICATION

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Photosensitizer

TRIS linker

PS — D + H+ + e−

PS* — DH

CO_2 Polyoxometalate

$CO2 + 2 H+ + 2 e- \longrightarrow CO + H2O$
or
$CO2 + 2 H+ + 2 e- \longrightarrow HCOOH$

Polyoxometalates*

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