A Bioinspired Molybdenum Catalyst for Aqueous Perchlorate Reduction

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Abstract

The detection of perchlorate (ClO_4^-) on and beyond Earth requires ClO_4^- reduction technologies to support water purification and space exploration. However, the reduction of ClO_4^- usually entails either harsh conditions or multi-component enzymatic processes. We developed a heterogeneous Mo−Pd/C catalyst from sodium molybdate to reduce aqueous ClO_4^- into Cl^- with 1 atm H_2 at room temperature. Upon hydrogenation by H_2/Pd, the reduced Mo oxide species and a bidentate nitrogen ligand (1:1 molar ratio) are transformed *in situ* into oligomeric Mo sites on the carbon support. The turnover number and frequency for oxygen atom transfer from ClO_x^- substrates reached 3850 and 165 h^{-1} on each Mo site. This simple bioinspired design yielded a robust water-compatible catalyst for the removal and utilization of ClO_4^-.

Perchlorate (ClO_4^-) is a pervasive water contaminant on Earth (*1, 2*) and a major salt component in the surface soil on Mars (*3, 4*). Because the uptake of ClO_4^- through water and food can cause thyroid gland malfunction, ClO_4^- levels in the drinking water are regulated. NASA has also identified Martian ClO_4^- as both a potential hazard to humans and an oxygen source to supply exploration activities (*5*). However, ClO_4^- is highly inert, so that it is widely used for ionic strength adjustment in various chemical systems. The oxidizing power of ClO_4^- has been primarily utilized via rocket fuels or munitions (*1*). Here, we report on a simple yet highly active heterogeneous Mo−Pd catalyst that can reduce aqueous ClO_4^- into Cl^- with 1 atm H_2 at room temperature.

Microbes can use ClO_4^- for respiration (Fig. 1A) (*6, 7*). In the multifactor metalloenzyme system (Fig. 1B), a Mo co-factor biosynthesized from molybdate (*8*) and amino acid residues mediate the oxygen atom transfer (OAT) (*9*) from ClO_4^- (*10*). The $Mo^{IV/VI}$ redox cycling (Fig. 1C) is sustained by the electron transfer from H_2 or acetate via multiple Fe-S clusters, *heme* complexes, and electron shuttle compounds (*11*). Such complexity in biological systems challenges the design of an artificial ClO_4^- reduction system, especially in aqueous phase under ambient conditions. For example, ClO_4^- reduction by a Fe complex relied on hydrogen bonds in the secondary coordination sphere (Fig. 1D) and thus required the use of an anhydrous medium (*12, 13*). Furthermore, a single-function metal complex or isolated reductase needs special electron donors (e.g., methyl viologen, hydrazine, ferrocene, and phosphine) to sustain the redox cycle of the OAT metal (*12, 14, 15*). Therefore, a robust catalyst that can reduce aqueous ClO_4^- with H_2 is highly desirable (*16, 17*).

In our bioinspired design (Fig. 1F), Pd/C is used as the catalyst platform. The porous carbon mimics the protein pocket of the enzyme that accommodates the OAT metal site. The Pd^0 nanoparticles simplify the enzymatic electron transfer chain by directly harvesting electrons from H_2. Then the key task was to construct a highly active Mo site from molybdate ($Mo^{VI}O_4^{2-}$), the

same Mo source for the biosynthesized Mo co-factors (*8*). Polyoxometalates of aqueous molybdate (*18*) were readily adsorbed onto Pd/C within 30 min (fig. S1). The resulting heterogeneous MoO_x−Pd/C showed rapid reduction of ClO_3^- (*19*) but had negligible activity with ClO_4^-. Hence, we sought to substantially enhance the OAT activity of surface Mo sites by incorporating an organic ligand. Because biomimetic thio-coordinated Mo complexes are typically water- and oxygen-sensitive, we attempted to prepare active Mo sites *in situ* by simultaneously adding molybdate and neutral nitrogen ligands (*L*) in the water suspension of Pd/C under 1 atm H_2. This simple strategy achieved highly active ClO_4^- reduction by a series of (*L*)MoO_x−Pd/C catalysts (Table 1, figs. S2 and S3).

In general, aromatic bidentate ligands led to significantly higher ClO_4^- reduction activities than amines and monodentate pyridines. Bipyridine (*bpy*) was superior to phenanthroline and other aromatic ligands containing an imidazoline or oxazoline half moiety (Table 1, entries 17−19). Ligands with steric hindrance on the *ortho* positions (Table 1, entries 8, 9, and 20) and with a strain on the *bpy* backbone (Table 1, entry 22 versus 21) resulted in low activities. Electron-donating groups on the *para* positions (*20*) further enhanced the activity. At ambient temperature and pressure, ClO_4^- reduction by the [$(NH_2)_2bpy$]MoO_x−Pd/C catalyst (Table 1, entry 6) outperformed all abiotic catalysts reported to date (table S1). The chlorine balance was closed by ClO_4^- and Cl^-, indicating a negligible buildup of ClO_x^- intermediates (Fig. 2A). The optimal molar ratio between $(NH_2)_2bpy$ and Mo was 1:1 (Fig. 2B), and the optimal Mo content in the catalyst was 5 wt% (Fig. 2C). The reuse of the catalyst for ten times did not cause a noticeable loss of activity (Fig. 2D, fig. S4). During the ClO_4^- reduction, the ratios of leached Mo and $(NH_2)_2bpy$ into water were <1.5% and <0.2% of the total amount in the catalyst, respectively (Fig. 2E). The apparent 1st-order kinetics with 0.01−1 mM ClO_4^- and 0th-order kinetics at 1−100 mM ClO_4^- (figs. S5 and S6) support the

Langmuir–Hinshelwood model for heterogeneous catalysis (See Supplementary Text for kinetic modeling and mass transfer analysis). Notably, a 0.2 g/L loading of the catalyst reduced 99.99% of 100 mM ClO_4^- (~10 g/L) within 48 h (fig. S5c). Due to the high oxidative stress caused by ClO_x^- intermediates (*10, 21*), complete reduction of 100 mM ClO_4^- in water has not been reported by either microbial or abiotic systems. Assuming the Mo sites catalyzed the OAT with both ClO_4^- and ClO_x^- intermediates, the turnover number (TON) for the single batch and the initial turnover frequency (TOF_0) reached 3850 and 165 h^{-1}, respectively, for each Mo atom.

While enzymes use amino acid residues to facilitate the reduction of metal-bound oxyanions (*10, 22*), the carbon-supported catalyst needs external protons to enable the reaction (*19, 20*). The optimal activity was afforded by 1 mM H^+ (pH 3.0 by H_2SO_4). The reduced performance at a lower pH (Fig. 2F) was probably caused by the protonation of amino groups on $(NH_2)_2bpy$. In the presence of 0.1 M Cl^-, 2.0 M Cl^-, and 1.0 M SO_4^{2-}, the catalyst retained 57%, 5%, and 36% of activity, respectively (fig. S7 and table S2), showing promise for the reduction of ClO_4^- in brine solutions produced from ion-exchange or from reverse osmosis for water treatment (*1*). Furthermore, exposing the catalyst suspension to air did not cause irreversible deactivation. The same ClO_4^- reduction activity was recovered after resuming H_2 supply (fig. S8a), suggesting that the *in situ* prepared catalyst can be handled in air. In comparison, the Re−Pd/C catalyst using the pre-synthesized Re^V precursor (Fig. 1E) (*23*) was highly sensitive to air and would irreversibly deactivate (fig. S8b) (*24, 25*).

X-ray photoelectron spectroscopy (XPS) characterization identified the reduction of Mo^{VI} precursor into multiple oxidation states (+VI, +V, +IV, +III and +II) (Fig. 3A versus 3B). Air exposure reoxidized the low-valent species to Mo^V and Mo^{VI} (Fig. 3C). For the reduced bulk catalyst sample, Mo K-edge X-ray absorption near-edge structure (XANES) spectroscopic

analysis found the average valence of Mo to be 4.3 from the edge energy of 20011.7 eV (Fig. 3D and fig. S9) (*26*). Fitting of the extended X-ray absorption fine structure (EXAFS) spectra found two major atomic shells for Mo−O (1.99 ± 0.03 Å) and Mo−Mo (2.57 ± 0.02 Å) (Fig. 3E, table S3, and fig. S10). This short Mo−Mo distance, in comparison to the value of 3.4 Å in Mo^{VI} oxide clusters (*26*), indicates the reduction of polymeric molybdate to Mo^{IV} by Pd-activated H_2 (*19*). The Mo−Mo coordination number (CN, 0.9 ± 0.5) suggests the heterogeneity of the surface Mo species as a mixture of monomers (CN = 0), dimers (CN = 1), and polymers (CN > 1).

Notably, the use of $(NH_2)_2bpy$ ligand changed the structure and activity of MoO_x in the catalyst. Without the ligand, the MoO_x−Pd/C catalyst could not reduce ClO_4^-, and the highest ClO_3^- reduction was achieved with only 0.5 wt% of Mo (fig. S11). Thus, the additional 4.5 wt% of Mo in a 5 wt% MoO_x−Pd/C catalyst acted as the structural building block of polymeric MoO_x clusters rather than catalytic sites. The CN for Mo−Mo in MoO_x−Pd/C (1.7 ± 0.6, table S3) also indicated the dominance of polymeric MoO_x clusters (*19*). In stark comparison, the ClO_4^- reduction activity of $[(NH_2)_2bpy]MoO_x$−Pd/C showed a linear increase until reaching 5 wt% of Mo. Thus, most Mo atoms acted as catalytic sites, and the most probable structure is an oligomer with one $(NH_2)_2bpy$ coordinating with each Mo (Fig. 2B). The elevated sensitivity with concentrated Cl^- upon the use of $(NH_2)_2bpy$ (table S2) also corroborates the altered structure of MoO_x by the organic ligand. A representative dimer structure (Fig. 3F) is proposed based on the reported crystal structure of $Mo^{VI}_2O_6[(tBu)_2bpy]_2$, a byproduct from the hydrothermal reaction using MoO_3 and 4,4'-$(tBu)_2bpy$ (*27*). Such a structure allows for multi-valent transformation of Mo between +VI and +II (Fig. 3B).

Scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectrometry (EDS) element mapping images indicate the ubiquitous distribution of Mo and N on

either carbon support or Pd^0 nanoparticles (Figs. 3G−3J and figs. S12−S14). The poor EXAFS fittings including Mo−Pd bonding (table S4) suggest isolated aggregation and distinct roles of Mo sites (OAT for ClO_x^- reduction) and Pd nanoparticles (electron transfer from H_2). However, the hydrogenation reaction is necessary to transform the polymeric Mo^{VI} precursors (*19*) and the free ligand into specific $[(NH_2)_2bpy]MoO_x$ structures to be reactive with ClO_4^-. For example, our cyclic voltammetry studies on the $[(NH_2)_2bpy]MoO_x/C$ material (without Pd^0 nanoparticles) between 0.37 and −1.1 V (versus the reversible hydrogen electrode) did not observe ClO_4^- reduction (fig. S15) but instead showed the reduction peaks of MoO_x and $(NH_2)_2bpy$ ligand (fig. S16). The potential allows the reduction of Mo^{VI} into Mo^V, Mo^{IV}, and Mo^{III} (*28, 29*), but the $[(NH_2)_2bpy]MoO_x$ clusters formed from the electrochemical reduction (*26*) were probably in different structures and thus not reactive with ClO_4^-.

The rapid and robust ClO_4^- reduction by a series of $(L)MoO_x$−Pd/C catalysts can be attributed to three major mechanisms similar to the microbial reduction process. First, the OAT energy barrier is lowered by the organic ligand (substituted *bpy* versus pterin in the Mo co-factor). Second, the redox cycling of Mo is sustained by the electron transfer from H_2 (enabled by the Pd^0 nanoparticle versus multiple biological metal factors). Third, the Mo-bound ClO_4^- requires the activation via protonation (externally added acid versus amino acid residues in the enzyme pocket). Mechanistic insights of this study highlight a strategy for designing bioinspired systems with common chemicals and simple approaches. Water-compatible heterogeneous catalyst systems will advance environmental and energy technologies for the removal and utilization of ClO_4^-.

Supplementary Materials:

Materials and Methods
Supplementary Text
Figures S1-S16
Tables S1-S4
References (*30-45*)

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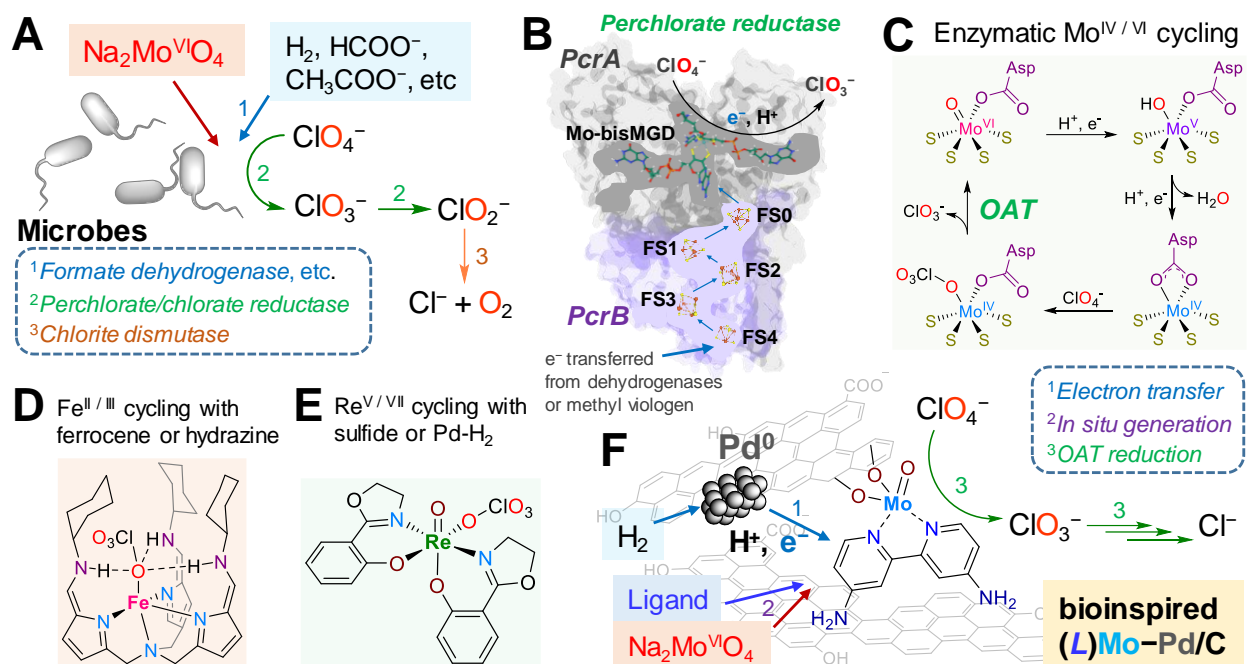
Fig. 1. Comparison of microbial and abiotic systems for perchlorate reduction. (**A**) Microbial process for ClO_4^- reduction; (**B**) electron transfer and metal centers in perchlorate reductase (Pcr); (**C**) proposed redox cycling of the Mo co-factor in reference (*10*); (**D**) a reported bioinspired iron complex for ClO_4^- reduction; (**E**) a reported rhenium complex for ClO_4^- reduction; (**F**) the general working mechanism of the new (*L*)MoO_x−Pd/C catalyst in this study.
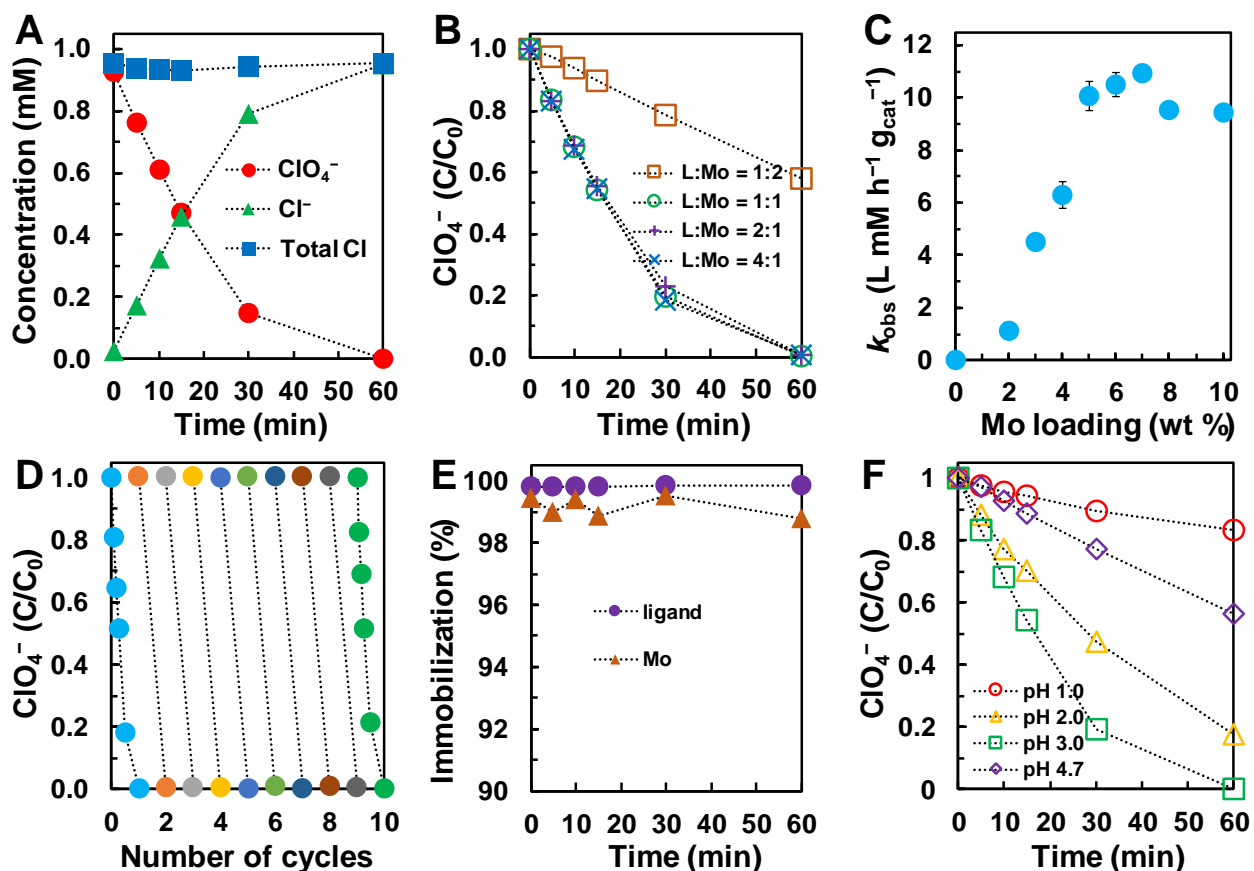
Fig. 2. Kinetics data. **(A)** Chlorine balance during the reduction of ClO_4^-; **(B)** the effect of the different molar ratios of $(NH_2)_2bpy$:Mo; **(C)** the effect of Mo content in the catalyst (y-axis: apparent 0th-order rate constant divided by the catalyst loading); **(D)** performance for ten spikes of 1 mM ClO_4^-; **(E)** the ratio of immobilized ligand and Mo during the reduction of ClO_4^-; **(F)** the effect of solution pH. Default reaction conditions: 0.2 g L^{-1} catalyst (5 wt% Mo in 5 wt% Pd/C, molar ratio of $(NH_2)_2bpy$:Mo=1:1), 1 mM ClO_4^-, pH 3.0, 1 atm H_2, 20 °C.
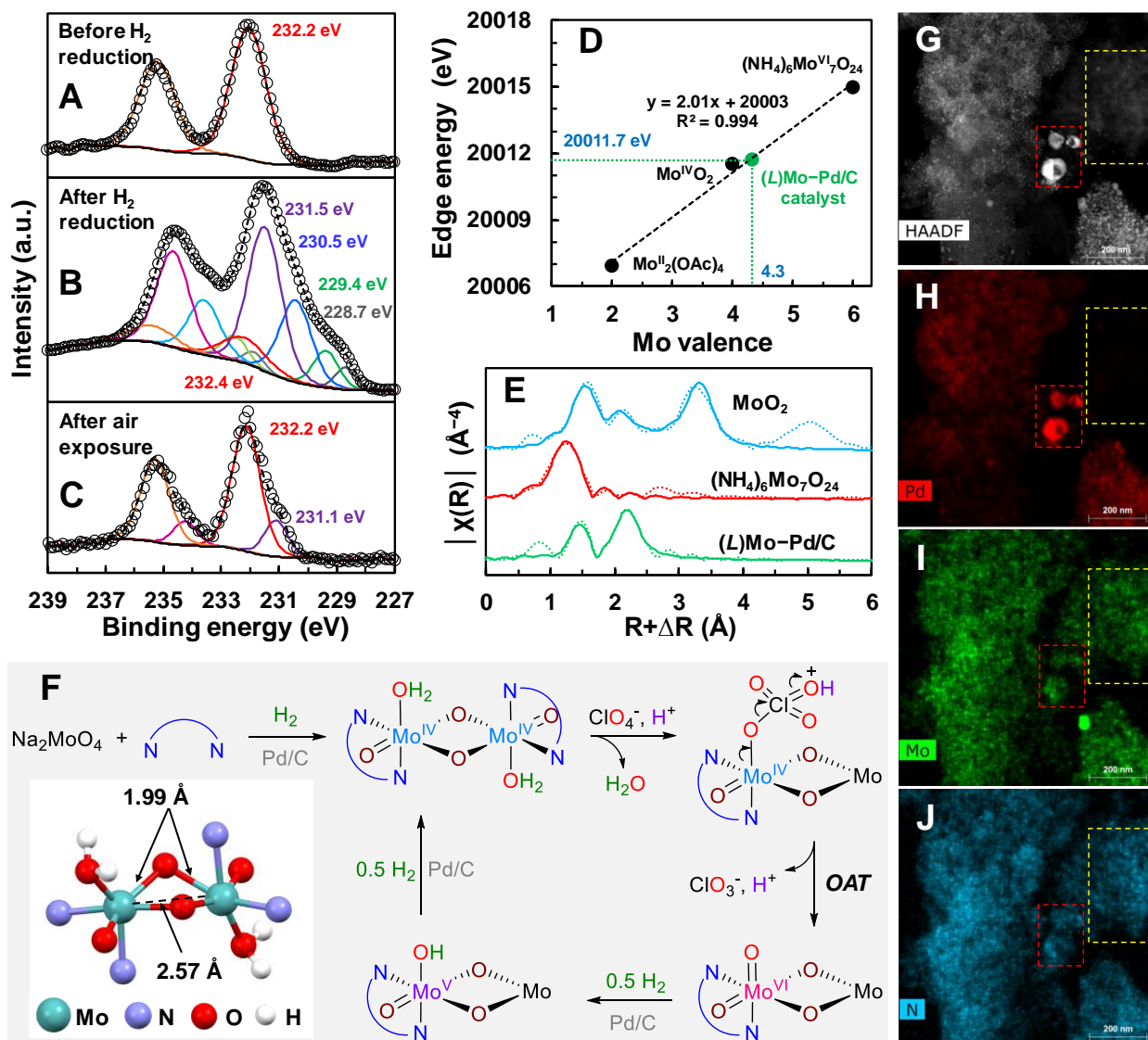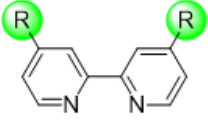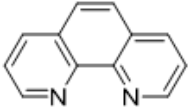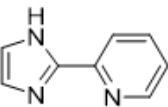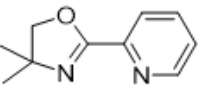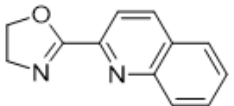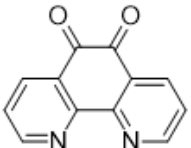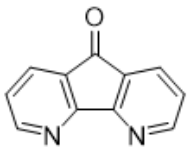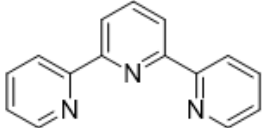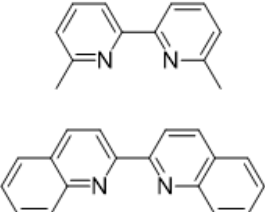
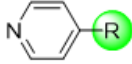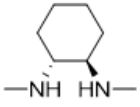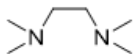**Fig. 3.** Characterization data and proposed reaction mechanisms. **(A−C)** Mo 3d XPS spectra (empty dots) and fits (solid lines) of the $[(NH_2)_2bpy]MoO_x$−Pd/C catalyst; **(D)** the correlation between Mo K-edge XANES energies and valences for the catalyst and Mo references; **(E)** the EXAFS Fourier transforms (dotted lines) and their fits (solid lines); **(F)** a proposed structure of the reduced $[(NH_2)_2bpy]MoO_x$ species and one representative redox transformation for the catalytic reduction of ClO_4^-. **(G−J)** HAADF-STEM imaging of the $[(NH_2)_2bpy]MoO_x$−Pd/C catalyst and EDX mapping of Pd, Mo, and N. The two dotted areas show the heterogeneity of $[(NH_2)_2bpy]MoO_x$ species immobilized on both carbon support and Pd particles.

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Table 1. Perchlorate Reduction Activity of Mo−Pd/C Catalysts Enabled by Various Nitrogen Ligands.[a]

entry	ligand	TOF$_0$ (h^{-1})[b]	entry	ligand	TOF$_0$ (h^{-1})[b]
	4,4'-R-substituted 2,2'-bipyridine		17	1,10-phenanthroline	3.1
1	R = H	14.3			
2	R = Me	12.4	18	imidazole-pyridine	4.6
3	R = OH	11.7			
4	R = OMe	20.8	19	dimethyl-oxazoline-pyridine	2.8
5	R = NMe$_2$	53.9			
6	R = NH$_2$	106	20	oxazoline-quinoline	0.31
7	R = Cl	0.63			
8	6,6'-dimethyl-2,2'-bipyridine	0.78	21	1,10-phenanthroline-5,6-dione	11.2
9	2,2'-biquinoline	0.13			
	4-R-substituted pyridine		22	indeno-diazafluorenone	0.40
10	R = H	0.16			
11	R = OH	0.16			
12	R = NH$_2$	0.090			
13	R = NMe$_2$	0.79			
14	cyclohexane-1,2-diamine	0.43			
15	ethane-1,2-diamine	0.18			
16	N,N,N',N'-tetramethylethylenediamine	0.22	23	2,2':6',2''-terpyridine	0.85

[a]Reaction conditions: 1 mM ClO$_4^-$ in water, 0.5 g L^{-1} catalyst (5 wt% Mo and 5 wt% Pd on carbon), molar ratio of Ligand:Mo = 1 (bidentate) or 2 (monodentate), pH 3.0, 1 atm H$_2$, 20°C. Entries 5 and 6 used 0.2 g L^{-1} catalyst.

[b]Calculated using the degradation of the first 5% of 1 mM ClO$_4^-$ and four OAT cycles to reduce each ClO$_4^-$ into Cl$^-$.