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Tunable Molecular MoS₂ Edge-Site Mimics for Catalytic Hydrogen **Production**

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Supporting Information

ABSTRACT: Molybdenum sulfides represent state-of-the-art, non-platinum electrocatalysts for the hydrogen evolution reaction (HER). According to the Sabatier principle, the hydrogen binding strength to the edge active sites should be neither too strong nor too weak. Therefore, it is of interest to develop a molecular motif that mimics the catalytic sites structurally and possesses tunable electronic properties that influence the hydrogen binding strength. Furthermore, molecular mimics will be important for providing



mechanistic insight toward the HER with molybdenum sulfide catalysts. In this work, a modular method to tune the catalytic properties of the S-S bond in $MoO(S_2)_2L_2$ complexes is described. We studied the homogeneous electrocatalytic hydrogen production performance metrics of three catalysts with different bipyridine substitutions. By varying the electron-donating abilities, we present the first demonstration of using the ligand to tune the catalytic properties of the S-S bond in molecular MoS₂ edge-site mimics. This work can shed light on the relationship between the structure and electrocatalytic activity of molecular MoS₂ catalysts and thus is of broad importance from catalytic hydrogen production to biological enzyme functions.

INTRODUCTION

Electrochemical and photoelectrochemical water splitting are promising ways to store energy from intermittent sources (i.e., wind and solar) in the form of hydrogen.^{1,2} Hydrogen is ideal because of its high energy density and potential utilization without carbon emissions.^{3,4} Water splitting can be divided into two half reactions: the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), both of which need catalysts to reduce the overpotential, thereby increasing energy efficiencies. The best HER electrocatalyst to date is well-known to be platinum (Pt), which has a near-zero overpotential.

Recent advances have revealed that transition-metal chalcogenides, most notably MoS_x (x = 2-3), would be promising and inexpensive alternatives to Pt for electrochemical generation of hydrogen from water. $^{5-12}$ The catalytic activity of MoS₂ materials is thought to be localized to rare edge sites, where disulfide linkages or triangular MoS₂ units are exposed, and the bulk basal plane is inert.^{7,13} The use of homogeneous electrocatalysts mimicking these rare edge sites is an attractive approach because the density of the active sites can be maximized. In addition, molecular mimics can be studied with a variety of techniques and modified synthetically to systematically tune the catalytic properties. In 2012, Karunadasa and coworkers demonstrated that a molecular MoS₂ edge-site mimic performed well for homogeneous catalytic hydrogen generation.¹⁴ Furthermore, Kibsgaard and co-workers, in 2014, found inspiration from chemistry outlined in the late 1970s^{15,16} and synthesized $[Mo_3S_{13}]^{2-}$ nanoclusters that exhibited excellent HER activity in a heterogeneous system.¹¹ Examples of Mo-Sbased molecules and clusters that mimic the triangular MoS₂

edge sites and catalytic activity for HER are limited to the pioneering work described above.^{11,14}

In this work, we describe a series of Mo-S molecular catalysts based on a $MoO(S_2)_2L_2$ structural motif that show electrocatalytic activity for HER. The MoS₂²⁻ moieties mimic the terminal edges in MoS₂ that are active sites for HER. Little work has been done with $MoO(S_2)_2L_2$,^{17,18} but the chemistry of similar peroxo complexes, $MoO(O_2)_2L_2$, is well developed, owing to their utility as oxidation catalysts for organic transformations.^{19–25} Accordingly, the library of known $MoO(O_2)_2L_2$ is large.^{24,25} Herein is described a general synthetic strategy, where peroxo (O_2^{2-}) in $MoO(O_2)_2L_2$ is exchanged with persulfide (S_2^{2-}) to afford $MoO(S_2)_2L_2$. The unique S_2^{2-} ligand-exchange method is a powerful method to produce many interesting $MoO(S_2)_2L_2$ complexes, three of which are highlighted in this study: $MoO(S_2)_2bpy-R$ [bpy-R = 2,2'-bipyridine (bpy, 1S), 4,4'-di-*tert*-butyl-2,2'-bipyridine (bpyt-butyl, 2S), and 4,4'-dimethoxy-2,2'-bipyridine (bpy-OMe, **3S**); Figure 1]. The three MoS_2 edge-site mimetic complexes were synthesized open to air, in two steps, from low-cost materials and aqueous solvent: MoO_3 , H_2O_2 , bpy, $(NH_4)_2S$, and S₈. No advanced synthetic techniques or special equipment is thus necessary for the synthesis of 1S-3S.

Formation of a S-H bond is the first step in the proposed pathway for electrocatalytic proton reduction at MoS₂ nanoparticle edge sites.⁵ We sought to utilize the electron-donating properties of modified bpy ligands in 1S-3S to tune the

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Figure 1. Peroxo complexes 1-3 were first synthesized and then exposed to sulfurizing conditions to obtain 1S-3S. The three MoS₂ edge-site mimetic complexes were synthesized open to air, in two steps, from low-cost materials and aqueous solvent: MoO₃, H₂O₂, bpy, (NH₄)₂S, and S₈. No advanced synthetic techniques or special equipment is necessary for the synthesis of 1S-3S.

electron density of the Mo^{VI} center, which would then influence the Lewis basicity of the $S_2^{2^-}$ ligands. Herein we report the electrocatalytic hydrogen evolution performance metrics of **1S–3S**. Both acid-independent rate constants for proton reduction and overpotentials of **1S–3S** vary depending on the substitution on bpy. Herein is described the first demonstration of using commercially available substituted bpy ligands to tune the catalytic properties of molecular MoS₂ edge-site mimics.

RESULTS AND DISCUSSION

Synthesis. As shown in Figure 1, we first synthesized the peroxo complexes 1–3 and utilized the thiophilicity of Mo by exposing 1–3 to sulfurizing conditions to obtain the persulfido complexes 1S–3S. In comparison to prior reports of mixing MoO_4^{2-} and aqueous $S_x^{2,17}$ our new ligand-exchange method reduces complex side reactions because the Mo center and the ancillary bpy ligand have been preorganized in the peroxo complexes. Moreover, the chemistry of molybdenum peroxo complexes, such as 1–3, is well developed, and the library of known $MoO(O_2)_2L_2$ complexes is large because of the ease of synthesis.^{24,25} Therefore, we think our new method is widely applicable.

The utility of the new $S_2^{2^-}$ ligand-exchange method can be appreciated by describing the procedure for the synthesis of **1S**-3**S**. We first heated a slurry of molybdenum(VI) oxide (MoO₃) in an aqueous hydrogen peroxide solution in air to obtain a yellow solution of MoO(O₂)₂(H₂O)₂, which is stable on the shelf for days.²⁶ The addition of a dilute aqueous solution of MoO(O₂)₂(H₂O)₂ to methanol (MeOH) solutions of L (L = bpy, bpy-*t*-butyl, bpy-OMe) affords the microcrystalline products 1-3 in greater than 90% yield. We then added 1-3 to an ammonia polysulfide solution. Complexes 1-3 were insoluble in the ammonia polysulfide solution; however, the solid immediately darkened to a dark red/purple solid. Stirring the slurry at room temperature for 3 h resulted in incomplete conversion. Heating the slurry at 60 °C for 1 h afforded a purple powder, which was **1S**-**3S** (Figures S1 and S2), as measured by ¹H NMR, mass spectrometry (MS), Fourier transform infrared (FTIR), UV–vis, and X-ray crystallography. The overall reaction scheme for the novel $S_2^{2^-}$ ligand-exchange procedure used in the synthesis of **1S–3S** is outlined in Figure 1.

Characterization. Single crystals were grown and structure determinations were carried out on **1S**–**3S**. Crystals of **1S** were grown by first dissolving the purple solid in a boiling solution of *N*,*N*-dimethylformamide (DMF; bp 153 °C) in air. Slow evaporation of DMF afforded crystals of **1S**, whose unit cell parameters matched the literature.¹⁷ It is worth noting the stability of complex **1S** in a boiling solution of DMF in air. Both **2S** and **3S** were grown by slow diffusion of toluene into DMF solutions at room temperature. Both **2S** and **3S** (Figure 2) are similar in structure to the previously reported **1S** and other mononuclear tungsten and molybdenum sulfide complexes.^{17,27} Selected interatomic distances are given in Table S1. Each S₂^{2–}



Figure 2. X-ray crystal structures of **2S** and **3S**. Thermal ellipsoids are shown at 50% probability, and H atoms are omitted for clarity. Crystals of **1S** were grown as well, and the unit cell parameters matched the literature.¹⁷ The ability to affect the S–S moiety by simple ligand substitution will be important for future catalytic application.



Figure 3. ¹H NMR spectra of bpy-*t*-butyl, 2, and 2S in CDCl₃. The ¹H NMR spectrum of complex 2 exhibits eight different chemical environments of bpy-*t*-butyl, illustrating the different binding environments of the two N atoms. The spectra clearly illustrate the binding of the ligand, and the change in the environment upon sulfurization. ¹H NMR spectroscopy is thus a convenient method for the characterization of $MoO(S_2)_2L_2$ complexes.

ligand may be viewed as occupying two coordination sites. Therefore, these complexes may be viewed as heptacoordinated, pentagonal bipyramidal in structure, with the two S_2^{2-} ligands occupying four equatorial bonding positions. The bpy ligand bridges the axial and remaining equatorial sites. The oxo ligand (Mo=O) occupies the remaining axial site.

In these complexes, the Mo–N bond lengths involving the bpy N atoms show significant coordination differences. The Mo–N axial to the oxo ligand demonstrates a trans influence, with the axial Mo–N2 bond length 0.14 Å longer than the equatorial Mo–N1 bond length in **1S**, 0.12 Å longer in **2S**, and 0.12 Å in **3S**. Notably, the more electron-donating bpy ligands, bpy-*t*-butyl and bpy-OMe, display a slightly shorter bonding distance on the axial Mo–N bond. The shorter bonding distance between Mo and N in the axial position indicates that the stronger electron-donating ligands, bpy-*t*-butyl and bpy-OMe, display stronger binding character to the Mo center.

The Mo–S bond distances in complexes **1S–3S** of 2.35– 2.43 Å are similar to those reported for other MoS_2 complexes.^{14,28,29} Within all of these structures, the MoS_2 moiety forms a molecular triangle, akin to the disulfide linkages on MoS_2 nanoparticles attributed to HER activity. The Mo–S bond distances are consistent with single Mo–S bonds, and the S–S bonds of 2.04–2.06 Å are consistent with a single bond between the two S atoms.

A major advantage of molecular derivatives of MoS_2 edge-site mimics over nanoparticles is the ability to use traditional molecular characterization techniques, such as ¹H NMR, MS, FTIR, UV–vis spectroscopy, and X-ray crystallography, to probe the local structures. As an example, Figure 3 shows the ¹H NMR spectrum of complex 2, which exhibits eight different chemical environments of bpy-*t*-butyl (Figure 3), illustrating the different binding environments of the two N atoms. The different binding environments of the bpy-*t*-butyl ligand are consistent with the structure determined from X-ray crystallography. One can see that the exchange of O_2^{2-} for S_2^{2-} results in a 0.15 ppm shift downfield of H_A from 9.41 to 9.56 ppm. The remaining protons all showed an upfield shift, as expected from oxygen's increased ability to deshield protons relative to sulfur. Thus, as Figure 3 illustrates, ¹H NMR spectroscopy is a convenient method for the characterization of $MoO(S_2)_2L_2$ complexes.

Characterization of Reduction Processes. In this work, we propose that $MoO(S_2)_2L_2$ complexes are molecular models for the active sites of well-studied MoS_2 nanoparticles that are responsible for HER activity.^{3,4} The proper assignment of reductive processes is therefore crucial for continued study and utilization of the new family of MoS_2 molecular mimics. We hypothesize that the reduction of **1S–3S** proceeds through first reduction of the S–S moiety rather than the metal center.

The reduction potentials of complexes 1-3 and similar peroxo complexes have been studied in detail.³⁰ It has been reported that the O–O bond strengths in peroxovanadium, -chromium, -molybdenum, and -tungsten complexes are related to the reduction potentials. It was found that the O–O bond distance, as measured by FTIR, is linearly correlated with the reduction potential of the complexes. It is also worth noting that their study showed no correlation between the M==O frequencies and reduction potentials. Therefore, reduction of the d⁰ peroxo complexes was attributed to reduction of the O–O ligands, likely cleaving the O–O bond, resulting in irreversibility of the chemical process.

Borrowing from the lessons learned in the peroxo examples,³⁰ we sought to assign reductive processes in the cyclic voltammetry of 1S-3S. Cyclic voltamograms (CVs) of 2 mM solutions of 1S-3S in DMF, at a scan rate of 200 mV s⁻¹, with a glassy carbon (GC) working electrode, a graphite rod counter electrode, and a Ag/AgNO3 reference electrode are presented in Figure S3. The previously reported CV of 1S displayed an irreversible cyclic voltammetric response at -1.59V versus ferrocene $(Fc^{+/0})$, and constant-potential coulometry suggested that 1S underwent reduction in two one-electron steps.¹⁷ The CVs of 2S and 3S are similar to the CV of 1S, where an irreversible reduction peak is followed by another reduction peak at a slightly more negative potential (Figure S3). Density functional theory (DFT) calculations revealed that the first and second reductions result in an increase in the charge density around the S-S ligands and bpy, as illustrated by the increase in red color upon reduction (Figure 4). The calculations further showed a *decrease* in the charge density



Figure 4. Charge density plots as calculated by NPA showing that the first reduction is centered on the S–S ligand and the second reduction is both S–S- and bpy-centered. Red indicates an increase in negative charge and blue an increase in positive charge. The calculations showed that the first and second reduction of the S–S ligand resulted in the lengthening of the Mo–S1 and Mo–S4 bonds by 0.10 and 0.09 Å, respectively. There was little change in the S–S bonds for the first (0.009 Å) and second reduction (0.004 Å). Figure S4 details the change in the charge density for each reduction.

on the Mo center and little change on the O center relative to S. On going from the neutral to the 1- and 2- states, the percent change was greatest for the S–S ligands in 1S, as outlined in Figure S4. We conclude from the charge density plots, the irreversible behavior in the CV of 1S, and prior work on peroxo complexes that the reduction processes are primarily ligand-centered.

Recent work has demonstrated that complex reductive processes, both ligand- and metal-centered, may contribute to MoS_2 nanoparticle activity.^{13,31} A molecular MoS_2 mimic, where redox processes are S–S-centered, can help shed light on the fundamental mechanistic comprehension of the whole research field. The insight provided by the ligand-centered molecular mimics of MoS_2 , along with the metal-centered redox properties of pentapyridylmolybdenum(IV) disulfide,¹⁴ will provide complementary mechanistic details for MoS_2 nanoparticles.

Electrochemical Hydrogen Production. CVs of 2 mM solutions of 1S-3S in DMF, at a scan rate of 200 mV s⁻¹, with a GC working electrode and a Ag/AgNO₃ reference electrode, showed that the addition of trifluoroacetic acid (TFA) resulted in an increase of the cathodic current at the potential of the S-S reduction (Figure 5). Enhancement of the current in a single direction is characteristic of the electrocatalytic reduction of protons to hydrogen (HER). When a CV of 80 mM TFA in DMF with a GC working electrode is compared to CVs of 1S-3S under the same conditions, it is clear that proton reduction is not due to direct reduction on the GC working electrode (Figure S5). UV-vis spectra of 1S with varying equivalents of TFA showed no change in absorption, indicating that 1S-3S are stable in DMF in the presence of TFA (Figure S6). Headspace analysis via gas chromatography following controlled potential electrolysis confirmed that hydrogen was produced with a Faradaic efficiency of 83%. UV-vis spectra of the solution of 1S after controlled potential electrolysis and of



Figure 5. CVs of **1S**–**3S** in the presence of increasing concentrations of TFA (CF₃CO₂H). Enhancement of the current in a single direction is characteristic of electrocatalytic reduction of protons to hydrogen. Headspace analysis via gas chromatography following controlled potential electrolysis of **1S** confirmed that hydrogen was produced with a Faradaic efficiency of 83%. Acid-independent rate constants of 95, 246, and 227 s⁻¹ were found for **1S**–**3S**, respectively.

2S and **3S** after cyclic voltammetry experiments are presented in Figure S7. These spectra clearly demonstrate the excellent stability of **1S**–**3S** in the presence of up to 400 equiv of TFA and an applied potential.

Enough acid was added to enter the acid-independent regime, where the concentration of H^+ is sufficiently high that it is not depleted by the catalytic process during the course of the experiment and another elementary step beyond diffusion becomes rate-limiting in the catalytic cycle. Using data in this acid-independent regime, the rate constant for hydrogen evolution can be calculated from the expression given in eq 1

$$\frac{i_{\rm c}}{i_{\rm p}} = \frac{n}{0.4463} \sqrt{\frac{RTk}{F\nu}} \tag{1}$$

in which i_c is the catalytic current in the presence of acid, i_p is the current of the catalyst with no acid, ν is the potential scan rate, n is the number of electrons transferred (two for hydrogen evolution), R is the universal gas constant, T is the temperature, and F is Faraday's constant.^{32,33} Solving for k and using i_c/i_p from the acid-independent region for a scan rate of 200 mV s⁻¹, acid-independent rate constants of 95, 246, and 227 s⁻¹ were found for **1S**–**3S**, respectively.

We confirmed that electrocatalysis originated from a molecular species in solution. Following catalytic cyclic voltammetry, the working electrode was immersed in a fresh solution of TFA in DMF, without catalyst. In this solution, catalysis was not observed, indicating that the catalytically active species was homogeneously dissolved in solution and not confined to an ill-defined deposited nanoparticulate material at the electrode surface (Figure S8). A scan rate dependence study

was carried out with 1S, and acid-independent rate constants were calculated to be 107, 94, and 95 s⁻¹ at scan rates of 50, 100, and 200 mV s⁻¹, respectively (Figure S9). By contrast, complex 1, lacking the S–S moiety, was not stable in the catalytic conditions used for 1S–3S and showed decreased catalytic activity (Figure S10). Furthermore, DFT calculations were performed in order to probe possible reaction pathways for the HER. The Gibbs free energies of all reactants, intermediates, and products were calculated and used to propose possible reaction pathways. It is clear from the pathways probed that participation of the S–S moiety is thermodynamically more favorable than that of the oxo moiety (Mo=O) in the catalytic cycle (Figures S18–S25). Thus, the S–S moiety is necessary for efficient electrocatalytic HER.

DFT at the M06-L/6-31+G* level of theory (with a SDD pseudopotential basis set for the Mo atom and 6-31+G* for all other atoms) was employed to analyze the locations of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of 1S (Figure S9) in the gas phase. The HOMO is located exclusively on the S-S ligands in 1S, suggesting that in solution the S–S ligand will be the initial site of protonation. By providing a stronger electrondonating bpy ligand, the S-S moiety will then become more basic, making protonation more favorable and thereby improving the catalytic activity. We observed that the acidindependent rate constant varies with the electron-donating ability of the bpy ligand. The stronger the electron-donating ability of the various bpy ligands (bpy-OMe \approx bpy-t-butyl > bpy), the higher the acid-independent rate constant of the catalyst (rate constant $2S \approx 3S > 1S$). The similar rate constants for 2S and 3S are consistent with the similar electrondonating abilities of *t*-butyl and OMe when in the para position $(\sigma = -0.15 \text{ and } -0.27 \text{ for } t\text{-butyl and OMe, respectively}).^{34} \sigma$ represents the electron-withdrawing or -donating abilities of different substituents, as determined from linear free-energy relationships. The more negative the σ value, the more electron-donating the substituent. The tunability illustrated here is the first demonstration of using commercially available, substituted bpy ligands to tune the S-S ligand in a molecular MoS₂ edge site, thereby affecting the catalytic properties.

The electrochemical overpotential is an equally important metric for characterizing electrocatalysts as rate constants. The overpotential is essentially an activation energy for hydrogen production. Fourmond and co-workers developed a method for calculating the overpotential based on the potential required to attain half of the overall catalytic current in nonaqueous solvents.³⁵ Following this method, the overpotentials for **1S**–**3S** were calculated based on the potential of proton reduction of TFA in DMF and are summarized in Table 1.³⁶ The tunable, stable MoS_2 complexes presented in this work show comparable rate constants for hydrogen production and lower

Table 1. Table Summarizing the Reduction Potentials, RateConstants, and Overpotentials a

complex	$E_{\rm S-S}/E_{\rm bpy}~({\rm V~vs~Fc^{+/0}})$	rate constant (s^{-1})	overpotential (mV)
15	-1.63/-2.37	95	617
28	-1.71/-2.48	246	860
38	-1.77/-2.45	227	806

^{*a*}The first reduction (E_{S-S}) is assigned as mainly S–S-centered, and the second reduction (E_{bpy}) is assigned as bpy- and S–S-centered, as determined from the DFT charge density plots described above.

overpotentials, as the pentapyridylmolybdenum(IV) disulfide examples previously demonstrated.¹⁴

Conclusion. Herein we report a general and modular method to tune the catalytic properties of a new family of molecular MoS₂ edge-site mimics for homogeneous HER. The catalysts presented were synthesized in air, in two steps, from low-cost materials $[MoO_3, H_2O_2, bpy, (NH_4)_2S, and S_8]$, illustrating their scalability. We studied the electrocatalytic HER performance metrics of three novel catalysts and found that, by simply varying substitution on the bpy ligands, we were able to effect the S-S ligand, thereby tuning the rate constants for HER and the overpotentials. Tuning the basicity of the S-S ligand is important because formation of a S-H bond is the proposed first step in the pathway for electrocatalytic proton reduction at MoS₂ nanoparticle edge sites. Thus, the first demonstration of using the ligand to tune the S-S catalytic properties in molecular MoS₂ edge-site mimics was demonstrated.

METHODS

General Considerations. All reactions and operations were carried out open to air, in a well-ventilated hood. All commercially available reagents were of ACS-grade and were used without further purification. ¹H NMR spectra were recorded on a 400 MHz Bruker spectrometer and are reported relative to tetramethylsilane. Highresolution MS spectra were obtained on Bruker MicroTOF mass spectrometer from the mass spectrometry facility at The Ohio State University. Solid-state IR spectra were recorded using a PerkinElmer FTIR/mid-IR spectrometer. Cyclic voltammetry measurements were performed using a Gamry Reference 600 potentiostat. All voltammograms were obtained in a three-electrode cell under an argon atmosphere at room temperature. The working electrode was a GC disk (0.071 cm²), and a graphite rod was used as the auxiliary electrode. The experimental reference electrode was Ag/AgNO₃, and the measured potentials are reported versus $Fc^{+/0}$, as determined by recording with an internal reference of Cp2Fe/Cp2Fe^{+,37} The supporting electrolyte was 0.1 M ⁿBu₄NPF₆, and the scan rate was 200 mV s⁻¹.

Computational Methods. Electronic structure calculations were performed using *Gaussian 09* for complex **1S**.³⁸ Solvent effects were modeled using the polarizable continuum model, with DMF as the solvent.³⁹ Ground-state geometry optimizations were carried out using the M06-L exchange correlation functional.⁴⁰ The SDD energy consistent pseudopotential was used for the core electrons along with the SDD basis set for valence electrons of molybdenum, while the 6-31+G* basis set was used for all other atoms.^{41,42} Optimized structures were confirmed as local minima on the potential energy surface using vibrational frequency analysis. Effective atomic charges were calculated using natural population anyalsis (NPA).⁴³

X-ray Structure Determination. Details of the X-ray structure determination and crystallographic data are summarized in the Supporting Information. CCDC 1419903 and 1419904 contain the supplementary crystallographic data for complexes 2S and 3S. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk].

Representative Synthesis of $MoO(O_2)_2$ bpy-R (1–3). The following procedure was adapted from previous methods.²⁶ To a 50 mL roundbottomed flask was added MoO₃ (1 g, 7 mmol), followed by 20 mL of H₂O₂ (30% by weight solution). This mixture was heated at 60 °C until all solid dissolved (~2 h). The yellow solution was filtered and diluted to 100 mL, forming a 0.07 M solution of MoO(O₂)₂(OH₂)₂, which is stable for days in solution. Note that bpy-OMe was solubilized in MeOH by the addition of ~1 mL of 1 M HCl. The 0.07 M yellow solution was added to a MeOH solution of bpy (1.09 g, 7 mmol in 400 mL of MeOH). Care should be taken that at least 4 times the amount of MeOH is used. A yellow precipitate was immediately afforded. After stirring for 15 min at room temperature, the precipitate was collected by filtration and washed with copious amounts of water, MeOH, and diethyl ether to afford yellow microcrystalline needles.

 $MoO(O_2)_2 bpy$ (1). Yield: 2.1 g (90%). FTIR (KBr): 940 vs, 859 vs, 772 vs, 763 m, 667 m, 583m, 535 w, 526 w cm⁻¹. ESI-MS: m/z356.938 [M + Na⁺]. UV-vis [DMF; $\lambda_{abs,max}$ (nm)/ ε (M⁻¹ cm⁻¹)]: 265/5372, 315/13516, 365/810.

MoO(*O*₂)₂*bpy-t-butyl* (2). Yield: 750 mg (91%). FTIR (KBr): 940 vs, 931 w, 871 s, 862 vs, 853 s, 745 w, 658 w, 606 w, 589 m, 532 w cm⁻¹. ESI-MS: *m/z* 469.064 [M + Na⁺]. UV–vis [DMF; $\lambda_{abs,max}$ (nm)/ε (M⁻¹ cm⁻¹)]: 265/3485, 305/8632, 315/9084, 370/403. ¹H NMR (400 MHz, CDCl₃): δ 9.41 (m, 1H), 8.25 (dd, 1H), 8.23 (m, 1H), 7.95 (m, 1H), 7.79 (dd, 1H, *J* = 1.96 and 4.04 Hz), 7.37 (dd, 1H, *J* = 1.38 and 3.88 Hz), 1.53 (s, 9H), 1.36 (s, 9H).

 $MoO(O_2)_2$ bpy-OMe (3). Yield: 1.2 g (92%). FTIR (KBr): 948 vs, 850 vs, 836 s, 728 w, 666 m, 658 m, 588 s, 528 s cm⁻¹. ESI-MS: m/z 416.959 [M + Na⁺].

Representative Synthesis of $MoO(S_2)_2$ bpy-R (**15** and **35**). To a 50 mL round-bottomed flask was added 20 mL of a $(NH_4)_2S$ solution (40%) and a stir bar. To this light-yellow solution was added 3.75 g of S_8 . This mixture was stirred at room temperature until all S_8 was dissolved to afford a deep-red solution. To the deep-red solution was added **1** (500 mg, 1.5 mmol), which was insoluble. This slurry was stirred vigorously and heated at 60 °C for 1 h, during which time the yellow solid turned dark purple/black. The mixture was allowed to cool to room temperature before the solid was collected by filtration and washed with copious amounts of water, MeOH, CS₂ and diethyl ether to afford a purple powder.

 $MoO(S_2)_2 bpy$ (1S). Yield: 180 mg (30%). FTIR (KBr): 925 vs, 766 vs, 724 m, 649 w, 634 w, 540 s cm⁻¹. ESI-MS: m/z 420.847 [M + Na⁺]. UV-vis [DMF; $\lambda_{abs,max}$ (nm)/ ε (M⁻¹ cm⁻¹)]: 265/14418, 305/14841, 440, 1036, 485/1706, 570/1692. ¹H NMR (400 MHz, DMSO- d^6): δ 9.51 (m, 1H), 8.96 (m, 1H), 8.64 (m,1H), 8.50 (m, 1H), 8.10 (m, 1H), 8.05 (m, 1H), 8.0 (m, 1H).

MoO(S_2)₂*bpy-OMe* (**35**). Yield: 350 mg g (50%). FTIR (KBr): 922 vs, 889 w, 871 w, 832 s, 742 w, 574 w, 538 s cm⁻¹. ESI-MS: *m/z* 480.868 [M + Na⁺]. UV–vis [DMF; $\lambda_{abs,max}$ (nm)/ ε (M⁻¹ cm⁻¹)]: 265/9422, 290/8076, 430/426, 485/735, 570/708. ¹H NMR (400 MHz, DMSO- d^6): δ 9.22 (d, 1H, J = 6.60 Hz), 8.51 (d, 1H, J = 2.68 Hz), 8.08 (d, 1H, J = 2.48 Hz), 7.77 (d, 1H, J = 6.36 Hz), 7.68 (d, 1H, J = 2.68 and 3.92 Hz), 6.85 (dd, 1H, J = 2.52 and 3.88 Hz), 4.18 (s, 3H), 3.89 (s, 3H).

 $MoO(S_2)_2 bpy-t-butyl$ (25). (NH₄)₂S_x was prepared as described above. To the deep-red solution was added 2 (666.5 mg, 1.5 mmol), which is insoluble. This slurry was stirred vigorously and heated at 60 °C for 1 h, during which time the yellow solid turned dark purple/ black. The mixture was allowed to cool to room temperature before the solid was collected by filtration and washed with copious amounts of water and MeOH. The aqueous filtrate was discarded. The solid was washed with dichloromethane (DCM), affording a dark-purple filtrate and a brownish-yellow solid. The purple filtrate was concentrated and subjected to silica gel chromatography, eluting first with DCM and then DCM/MeOH (9:1). Slow evaporation of the purple fractions afforded a dark-purple/black powder.

Yield: 150 mg (20%). FTIR (KBr): 934 vs, 898 s, 856 s, 739 w, 604 w, 550 m, 541 s cm⁻¹. ESI-MS: m/z 532.973 [M + Na⁺]. UV–vis [DMF; $\lambda_{abs,max}$ (nm)/ ε (M⁻¹ cm⁻¹)]: 265/12606, 300/12198, 430/ 655, 480/1365, 560/1394. ¹H NMR (400 MHz, CDCl₃): δ 9.56 (d, 1H, J = 6.04 Hz), 8.26 (m, 1H), 8.07 (d, 1H, J = 5.80 Hz), 7.84 (m, 1H), 7.81 (dd, 1H, J = 2.00 and 4.04 Hz), 7.04 (dd, 1H, J = 1.84 and 3.96 Hz), 1.53 (s, 9H), 1.36 (s, 9H).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b00206.

Cyclic voltammetry data, selected bond distances, electronic potentials, peak currents, calibration curve, HOMO and LUMO orbitals, UV–vis, FTIR, and ¹H NMR spectra, DFT pathway investigation, and atomic coordinates (PDF)

X-ray crystallographic data of complex **2S** in CIF format (CIF)

X-ray crystallographic data of complex **3S** in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Lewis, N. S.; Nocera, D. G. Proc. Natl. Acad. Sci. U. S. A. 2006, 103 (43), 15729–15735.

(2) Mckone, J. R.; Lewis, N. S.; Gray, H. B. Chem. Mater. 2014, 26, 407-414.

(3) Benck, J. D.; Hellstern, T. R.; Kibsgaard, J.; Chakthranont, P.; Jaramillo, T. F. ACS Catal. 2014, 4, 3957–3971.

(4) Yan, Y.; Xia, B.; Xu, Z.; Wang, X. ACS Catal. 2014, 4, 1693–1705.

(5) Hinnemann, B.; Moses, P. G.; Bonde, J.; Jørgensen, K. P.; Nielsen, J. H.; Horch, S.; Chorkendorff, I.; Nørskov, J. K. J. Am. Chem. Soc. 2005, 127, 5308–5309.

(6) Kristensen, J.; Zhang, J.; Chorkendorff, I.; Ulstrup, J.; Ooi, B. L. Dalton Trans. 2006, No. 33, 3985–3990.

(7) Jaramillo, T. F.; Jørgensen, K. P.; Bonde, J.; Nielsen, J. H.; Horch, S.; Chorkendorff, I. *Science* **2007**, *317* (5834), 100–102.

(8) Jaramillo, T. F.; Bonde, J.; Zhang, J.; Ooi, B. L.; Andersson, K.; Ulstrup, J.; Chorkendorff, I. *J. Phys. Chem. C* **2008**, *112* (45), 17492–17498.

(9) Laursen, A. B.; Kegnæs, S.; Dahl, S.; Chorkendorff, I. Energy Environ. Sci. 2012, 5, 5577-5591.

(10) Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. Nat. Chem. **2013**, 5 (4), 263–275.

(11) Kibsgaard, J.; Jaramillo, T. F.; Besenbacher, F. Nat. Chem. 2014, 6 (3), 248–253.

(12) Huang, Z.; Luo, W.; Ma, L.; Yu, M.; Ren, X.; He, M.; Polen, S.; Click, K.; Garrett, B.; Lu, J.; Amine, K.; Hadad, C.; Chen, W.;

Asthagiri, A.; Wu, Y. Angew. Chem., Int. Ed. 2015, 54, 15181–15185. (13) Lassalle-kaiser, B.; Merki, D.; Vrubel, H.; Gul, S.; Yachandra, V.

K.; Hu, X.; Yano, J. J. Am. Chem. Soc. 2015, 137, 314-321.

(14) Karunadasa, H. I.; Montalvo, E.; Sun, Y.; Majda, M.; Long, J. R.; Chang, C. J. Science **2012**, 335 (6069), 698–702.

(15) Müller, A.; Krickemeyer, E.; Hadjikyriacou, A.; Coucouvanis, D. Inorg. Synth. 1990, 27, 47–51.

(16) Müller, A.; Bhattacharyya, G. R.; Pfefferkorn, B. Chem. Ber. 1979, 112, 778-780.

- (17) Chakrabarty, P. K.; Bhattacharya, S.; Pierpont, C. G.; Bhattacharyya, R. Inorg. Chem. **1992**, *31*, 3573–3577.
- (18) Gushchin, A. L.; Laricheva, Y. L.; Alferova, N. I.; Virovets, A. V.; Sokolov, M. N. J. Struct. Chem. **2013**, 54 (4), 752–758.
- (19) Schlemper, E. O.; Schrauzer, G. N.; Hughes, L. A. Polyhedron 1984, 3 (3), 377–380.
- (20) Chakravorti, M. C.; Ganguly, S.; Bhattacharjee, M. Polyhedron 1993, 12 (1), 55–58.
- (21) Zhu, W.; Li, H.; He, X.; Shu, H.; Yan, Y. J. Chem. Res. 2006, 2006 (12), 774-775.
- (22) Brito, J. A.; Gomez, M.; Muller, G.; Teruel, H.; Clinet, J. C.; Dunach, E.; Maestro, M. A. Eur. J. Inorg. Chem. 2004, 2004 (21),
- 4278–4285.
- (23) Carrasco, C. J.; Montilla, F.; Alvarez, E.; Mealli, C.; Manca, G.; Galindo, A. *Dalton Trans.* **2014**, 43 (36), 13711–13730.
- (24) Conte, V.; Floris, B. Dalton Trans. 2011, 40, 1419-1436.
- (25) Dickman, M. H.; Pope, M. T. Chem. Rev. 1994, 94 (3), 569–584.
- (26) Herrmann, W. A.; Thiel, W. R.; Kuchler, J. G. Chem. Ber. 1990, 123, 1953–1961.
- (27) McConnachie, C. A.; Stiefel, E. I. Inorg. Chem. 1999, 38 (5), 964–972.
- (28) Shin, J. H.; Savage, W.; Murphy, V. J.; Bonanno, J. B.; Churchill,
- D. G.; Parkin, G. J. Chem. Soc. Dalt. Trans. 2001, No. 11, 1732–1753.
- (29) Shin, J. H.; Churchill, D. G.; Bridgewater, B. M.; Pang, K.; Parkin, G. Inorg. Chim. Acta 2006, 359 (9), 2942–2955.
- (30) Bonchio, M.; Conte, F.; Di Furia, F.; Modena, G.; Moro, S.; Carofiglio, T.; Magno, F.; Pastore, P. *Inorg. Chem.* **1993**, *32*, 5797–5799.
- (31) Huang, Y.; Nielsen, R. J.; Goddard, W. A.; Soriaga, M. P. J. Am. Chem. Soc. 2015, 137 (20), 6692–6699.
- (32) Appel, A. M.; DuBois, D. L.; Rakowski DuBois, M. J. Am. Chem. Soc. 2005, 127 (36), 12717–12726.
- (33) Gan, L.; Groy, T. L.; Tarakeshwar, P.; Mazinani, S. K. S.; Shearer, J.; Mujica, V.; Jones, A. K. *J. Am. Chem. Soc.* **2015**, *137*, 1109–1115.
- (34) Ritchie, C. D.; Sager, W. F. Prog. Phys. Org. Chem. 1964, 2, 323–400.
- (35) Fourmond, V.; Jacques, P. A.; Fontecave, M.; Artero, V. Inorg. Chem. 2010, 49 (22), 10338–10347.
- (36) Fourmond, V.; Canaguier, S.; Golly, B.; Field, M. J.; Fontecave, M.; Artero, V. Energy Environ. Sci. 2011, 4 (7), 2417–2427.
- (37) Connelly, N. G.; Geiger, W. E. Chem. Rev. 1996, 96 (2), 877-910.
- (38) Frisch, M. J.; et al. *Gaussian 09*, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.
- (39) Miertuš, S.; Tomasi, J. Chem. Phys. 1982, 65 (2), 239-245.
- (40) Zhao, Y.; Truhlar, D. G. J. Chem. Phys. 2006, 125, 194101.
- (41) Andrae, D.; Häußermann, U.; Dolg, M.; Stoll, H.; Preuß, H. Theor. Chim. Acta 1990, 77, 123–141.
- (42) Frisch, M. J.; Pople, J. A.; Binkley, J. S. J. Chem. Phys. 1984, 80, 3265.
- (43) Reed, A. E.; Weinstock, R. B.; Weinhold, F. J. Chem. Phys. 1985, 83 (2), 735–746.