

# Photoinduced Generation of a Durable Thermal Proton Reduction Catalyst with *in situ* Conversion of $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$ to $\text{Mn}(\text{bpy})_2\text{Br}_2$

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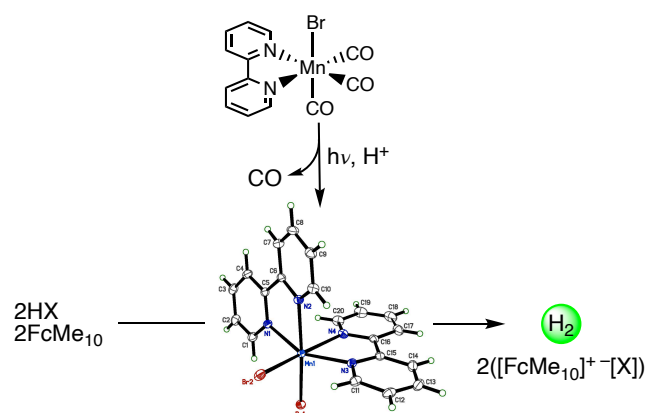
**ABSTRACT:** The conversion of protons to  $\text{H}_2$  is a critical reaction for the design of renewable fuel generating systems. Robust, earth abundant metal-based catalysts which can rapidly facilitate this reduction reaction are highly desirable.  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  generates an active catalyst for the proton reduction reaction upon photolysis at a high, directly observed  $\text{H}_2$  production rate of 1,300,000 turnovers per hour, with a low driving force for this reaction. Through the use of  $\text{FcMe}_{10}$  as an electron source, a proton source (triflic acid, 4-cyanoanilinium, or tosylic acid), and  $\text{MeCN}/\text{H}_2\text{O}$  as solvent, the thermal reaction at room temperature was found to proceed until complete consumption of the electron source. No apparent loss in catalytic activity was observed to the probed limit of 10,000,000 turnovers of  $\text{H}_2$ . Interestingly, a catalytically competent complex ( $\text{Mn}(\text{bpy})_2\text{Br}_2$ ), which could be isolated and characterized, formed upon photolysis of  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  in the presence of acid.

## Introduction

The efficient storage of energy in chemical bonds for use on demand is a critical step forward in renewable fuel production.<sup>1</sup> Proton reduction to  $\text{H}_2$  is a commonly pursued approach in the search for a chemical fuel that can be derived from an abundant resource such as water. If the hydrogen evolution reaction is paired with water oxidation, only  $\text{O}_2$  is generated as a stoichiometric waste.<sup>2</sup> Ideally, these catalytic processes would be driven by robust catalysts derived from earth abundant elements with fast rates of catalysis.<sup>3-4</sup> The catalysts should also durably operate with minimal driving force to avoid energetic losses.<sup>3</sup> Several reaction system designs coupling oxidative and reductive processes are reported in the literature surrounding electrochemical (EC) and photoelectrochemical cells (PEC), including those employing redox mediators which can alleviate relative rate concerns of the anodic and cathodic reactions.<sup>5-10</sup> PEC and EC catalyst performances can be efficiently probed through the study of half reactions using a stoichiometric chemical electron source or sacrificial electron donor (SED). This approach is common in the literature and has led to the discovery of molecular catalysts used to drive reductive reaction processes in EC and PEC systems.<sup>2-3, 11-21</sup> The use of an SED with reversible electron transfers (ETs) and no rapid chemical transformation step following the electron transfer step allows for the SED to potentially be used as a redox mediator in full PEC/EC systems.<sup>10</sup>

Manganese bipyridyl complexes have recently been shown to catalyze proton reduction reactions<sup>22</sup> in addition to  $\text{CO}_2$  reduction reactions.<sup>23-25</sup> Intriguingly, manganese tricarbonyl bromide complexes have been reported to dramatically change reactivity toward protons or  $\text{CO}_2$  based on the addition of water<sup>23</sup> and many of these complexes are reported under conditions which rigorously exclude light with red-light laboratory illumination being described in some literature instances as a needed precaution.<sup>11, 24, 26-29</sup> The use of dark conditions is interesting, since literature suggests that discrete

complexes are formed upon irradiation, which could be catalytically active in reduction reactions.<sup>30</sup> Whereas it can be difficult to isolate and confirm the identity of photogenerated compounds, the use of a photoinduced catalyst generation approach is convenient in that a simple to prepare starting complex can be transformed *in situ* to a new active catalyst for evaluation in the proton reduction reaction.



**Figure 1.** Photolytic CO dissociation from  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  (as shown by GC) to give  $\text{Mn}(\text{bpy})_2\text{Br}_2$  in the presence of protons.  $\text{Mn}(\text{bpy})_2\text{Br}_2$  is shown to facilitate the proton reduction reaction.

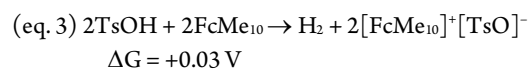
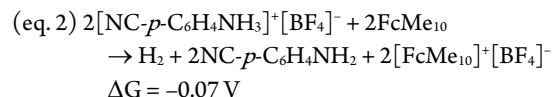
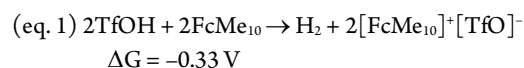
To probe the effects of light on  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  driven proton reduction reactions, a series of studies were performed using nuclear magnetic resonance (NMR), crystallography, infrared spectroscopy, electrochemical techniques, and thermal catalysis with an SED under varied conditions (Figure 1). For the thermal reduction reactions, a potential redox mediator, decamethylferrocene ( $\text{FcMe}_{10}$ ), was selected as the sacrificial electron donor. This electron source

**Table 1.** Electrochemical and optical data for Mn(bpy)<sub>2</sub>Br<sub>2</sub> and Mn(bpy)(CO)<sub>3</sub>Br.<sup>a</sup>

complex	$\lambda_{\text{max}}$ (nm)	$\lambda_{\text{onset}}$ (nm)	$E_{\text{red1 no H}^+}$ (V) peak   onset	$E_{\text{red2 no H}^+}$ (V) peak   onset	$E_{\text{red H}^+}$ (V) on- set	$i_{\text{cat}}/i_p$
Mn(bpy)(CO) <sub>3</sub> Br	422	485	---   -2.20	---   ---	-1.25	13
photolyzed Mn(bpy)(CO) <sub>3</sub> Br	302	325	-1.79   -1.65	-1.97   -1.85	-0.51	17
Mn(bpy) <sub>2</sub> Br <sub>2</sub>	371	375	-1.20   -0.90	---   ---	-0.55	23 (dark) 29 (light)

<sup>a</sup> All values are measured in MeCN.  $i_{\text{cat}}/i_p$  is calculated from the CV curve where  $i_{\text{cat}}$  is the peak current with TfOH present and  $i_p$  is the peak current without TfOH, with Mn(bpy)(CO)<sub>3</sub>Br measured at -1.75 V, the photoinduced catalyst measured at -0.80 V, and Mn(bpy)<sub>2</sub>Br<sub>2</sub> measured at -1.20 V.

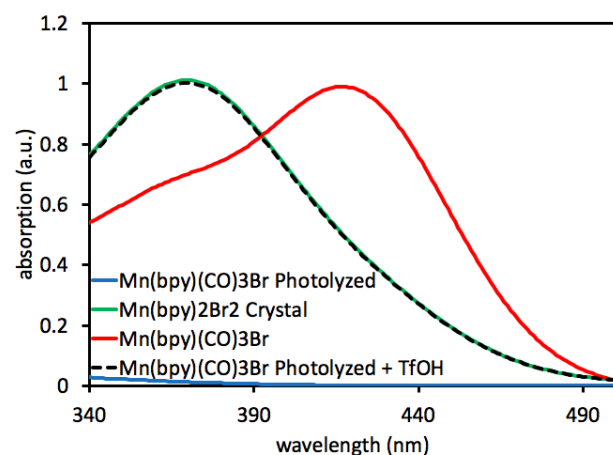
was selected as a strongly reducing electron donor ( $-0.51$  V versus  $\text{Fc}^+/\text{Fc}$ )<sup>14</sup> which leads to triflic acid in MeCN ( $2.6 \text{ p}K_a$ )<sup>31</sup> resulting in an estimated exothermic reaction via the Nernst equation ( $E = E^\circ - 0.059 \text{ p}K_a$ ) at a free energy of  $-0.33$  V when the standard reduction potential of  $\text{H}^+$  in MeCN is taken at  $-0.03$  V versus  $\text{Fc}^+/\text{Fc}$  (equation 1, Figure S1).<sup>32</sup> The use of tosylic acid ( $8.6 \text{ p}K_a$  in MeCN) results in an estimated slightly endothermic reaction at a free energy of  $+0.03$  V (equation 3).<sup>31, 33-34</sup> 4-cyanoanilinium ( $7 \text{ p}K_a$  in MeCN) was selected due to being reasonably well-behaved under anhydrous conditions with a comparable intermediate free energy ( $-0.07$  V) to the other acids in the reaction being probed (equation 2).<sup>31, 35</sup> The reactions could be driven at room temperature, and the use of proton and electron sources without large driving forces for proton reduction allows for the indirect probing of the activation energy barrier of the catalyst in powering these reactions. Given the dramatic effects water has shown in Mn catalyzed CO<sub>2</sub> reduction reactions, water in varying amounts is also investigated.<sup>23</sup>



## Results and Discussion

As expected based on literature precedent,<sup>30</sup> the exposure of Mn(bpy)(CO)<sub>3</sub>Br to ambient light in MeCN leads to the quantitative loss of 1 CO ligand, as confirmed by GC in our labs. During this time the solution of the complex changes from yellow to clear (Figures 2, S2 & S9, Table 1). This color change is diagnostic since Mn(bpy)(CO)<sub>3</sub>Br is known to dimerize to form [Mn(bpy)(CO)<sub>3</sub>]<sub>2</sub> in non-coordinating solvents, and [Mn(bpy)(CO)<sub>3</sub>]<sub>2</sub> has significant absorption spectrum features near 500 nm, 650 nm, and 850 nm.<sup>36</sup> These features are not present during ambient light photolysis in the presence of coordinating MeCN. Upon irradiation of Mn(bpy)(CO)<sub>3</sub>Br (red line), the absorption spectrum shows a quenching of the absorption at 422 nm and growth of the blue-shifted signal representative of the photolyzed, colorless solution (blue line in Figure 2; Figure S2). Upon the subsequent addition of TfOH, a signal at 370 nm arises, which is a new photogenerated complex (Figure 2). Additionally, <sup>1</sup>H NMR analysis of photolyzed Mn(bpy)(CO)<sub>3</sub>Br in CD<sub>3</sub>CN shows NMR signals in a broad shape with a high signal to noise possibly due to the poor solubility of the photolyzed complex in MeCN or the generation of a paramagnetic

complex with trace biproducts generating the observed signals (Figures S3 & S4). Addition of TfOH to the NMR mixture after photolysis gives a biproduct with sharp signals in the aromatic region not attributed with either the pre-photolyzed or post-photolyzed complex (Figure S5). No hydride signal was evident in the 0 to -70 ppm range. However, when TfOH, TsOH, or AcOH was added as an acid, the known complex Mn(bpy)<sub>2</sub>Br<sub>2</sub><sup>37</sup> could be obtained as x-ray



**Figure 2.** Absorption spectra of Mn complexes in MeCN before photolysis (red), after photolysis (blue), after photolysis with addition of TfOH (black), and after crystallization of Mn(bpy)<sub>2</sub>Br<sub>2</sub> (green).

quality crystals by evaporating the volatile components and taking the solids up in MeOH followed slow vapor diffusion of diethyl ether to give the crystalline complex at the top of the vial in high yield (>90% based on bpy, >45% based on Mn). The structure was confirmed by crystallography at 90K (Figure 1). Neither independently synthesized Mn(bpy)<sub>2</sub>Br<sub>2</sub> or that formed *in situ* gives paramagnetic <sup>1</sup>H NMR signals between 200 ppm and -200 ppm (Figure S6).

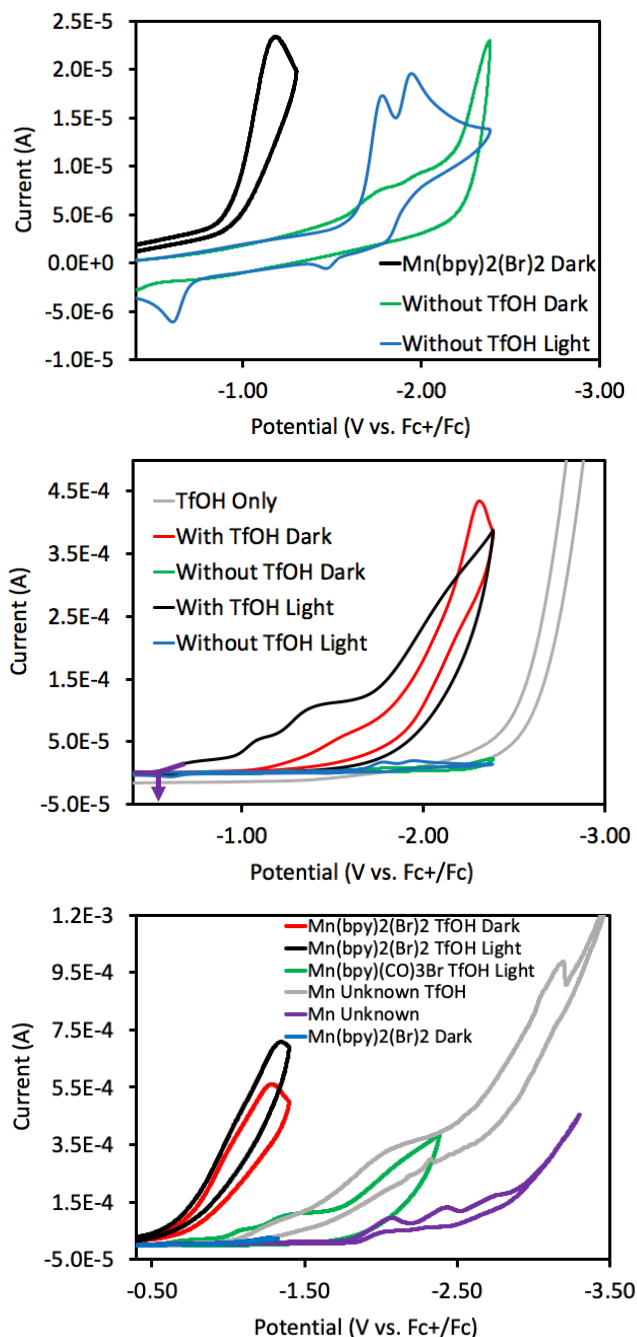
Absorption spectroscopy with Mn(bpy)<sub>2</sub>Br<sub>2</sub> (green line) shows a matched absorption curve to the sample of Mn(bpy)(CO)<sub>3</sub>Br exposed to light and TfOH (black dashed line), indicating the complex is formed readily under the reaction conditions in solution (Figure 2). It is not apparent why the addition of an acid source is required to obtain the Mn(bpy)<sub>2</sub>Br<sub>2</sub> complex. Additionally, attenuated total reflectance infrared spectroscopy (ATR-IR) confirms that the collected crystals no longer have an CO related signal in the 2100-1650 cm<sup>-1</sup> region (Figure S10 & S11). Consistent with only 1 CO being observed extruding from the reaction mixture via gas chromatography (GC), the IR spectrum of the remaining material in the mother liquor shows numerous CO signals with broadened features in the 2100-1650 cm<sup>-1</sup> region which may be due to either a number of species being present or the formation of Mn<sub>x</sub>(CO)<sub>y</sub>-clusters

(Figure S10 & S11). This material is observed to absorb in the UV region ( $<350$  nm) suggesting loss of any possible metal-ligand charge transfer bands due to loss of bipyridine (Figure S2). The IR spectrum further confirms near complete loss of bipyridine related features in the  $1600\text{--}1400\text{ cm}^{-1}$  region. The fate of the remaining Mn atom after 2  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  complexes are converted to  $\text{Mn}(\text{bpy})_2\text{Br}_2$  is not apparent. We note that 2 CO molecules are observed in the headspace via GC from 2  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  complexes. This leaves 4 CO groups and a Mn atom needed to balance the stoichiometry of the transformation shown in Figure S12.

Subjecting the crystallized  $\text{Mn}(\text{bpy})_2\text{Br}_2$  to the chemical reaction conditions found to be catalytically competent gave  $\text{H}_2$  at a very similar rate to photolyzed  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  although it should be noted that the rate of this system is likely SED solubility limited (see discussion below). Additionally,  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  and  $\text{Mn}(\text{bpy})_2\text{Br}_2$  prepared *via* independent methods gave the same aromatic NMR signals when the complex was exposed to TfOH and the reducing reagent  $\text{FcMe}_{10}$  (Figures S7 & S8). Although it cannot be confirmed that the signals observed are not a biproduct unrelated to catalysis, it is plausible that the paramagnetic  $\text{Mn}(\text{bpy})_2\text{Br}_2$  formed in the reaction mixture can be reduced to a diamagnetic  $\text{Mn}(\text{I})$  compound. Notably, all components necessary for catalytic  $\text{H}_2$  production are present once the reducing reagent and TfOH are added, which suggests the observed  $^1\text{H}$  NMR signals may either be a biproduct or the resting state of the catalyst. Importantly, both complexes appear to be doing the same chemistry given the same  $^1\text{H}$  NMR spectrum is arrived at after proton and reducing reagent are added.

Electrochemically, a significant change in the reduction potential of  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  is observed after light exposure in MeCN (Figure 3 top: green line (dark), blue line (light), Table 1). A shift of  $0.55$  V toward a more positive potential is observed with a first reduction potential peak of  $-1.79$  V for photolyzed  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  under argon (top: blue line). Even under conditions careful to exclude light, small amounts of the photolyzed product are present in the "dark" with  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$ .  $\text{Mn}(\text{bpy})_2\text{Br}_2$  shows a reduction wave onset near  $-0.9$  V with a reduction wave peak at  $-1.20$  V (top: black line). Introduction of a proton source (TfOH), leads to a shift toward more positive potentials for the  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  complex in the dark with an onset of  $-1.25$  V, and a peak potential observed at  $-2.24$  V after an initial plateau near  $-1.75$  V (middle: green line (without TfOH, red line (with TfOH))). The observed shift in electrochemical potential in the dark suggests an initial chemical reaction has taken place resulting in a new species with a more positive reduction potential. The observed onset of reduction is estimated to be an overpotential of  $1.07$  V as calculated from standard reduction potential of protons in MeCN solvent at  $-0.18$  V versus  $\text{Fc}^+/\text{Fc}$  with the  $\text{p}K_a$  of TfOH in MeCN taken at  $2.6$  and estimated through the Nernst equation (see above). The observed current enhancement is measured as an  $i_{\text{cat}}/i_p$  value of  $13$  at the first reduction's plateau ( $-1.75$  V).<sup>28, 38</sup> The photogenerated species shows a reduction potential onset near  $-0.51$  V versus  $\text{Fc}^+/\text{Fc}$  in the presence of TfOH (middle: black line). This corresponds to an overpotential of only  $0.32$  V and occurs  $0.75$  V more positive than that observed with  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  under otherwise identical conditions (middle: red line). Additionally, a large shift in reduction potential onset ( $1.14$  V) is observed when the CVs of photolyzed  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  with (middle: black line) and without (middle: blue line) TfOH are compared, which is consistent with the formation of a relatively electron deficient catalytically active complex upon the addition of TfOH. The observed current enhancement is representative of a  $17\times$

increase in current at the first reduction's plateau ( $-0.80$  V) (Figure 3, see Figures S13-S16 for additional CV data).

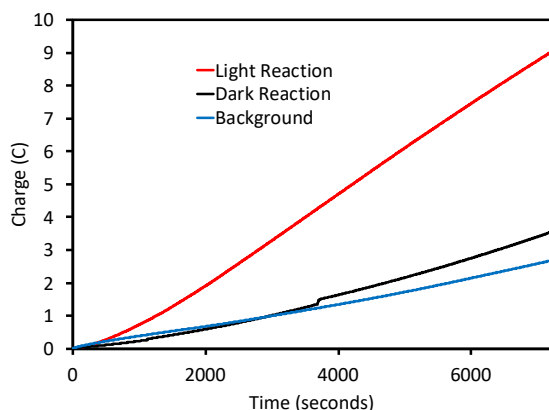


**Figure 3.** Top: CVs of  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  in the light or dark and  $\text{Mn}(\text{bpy})_2\text{Br}_2$ , all without TfOH. Middle: Cyclic voltammograms for  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  at  $1\text{ mM}$  ( $\mu\text{mol cat/mL MeCN}$ ) in the light or dark and with or without  $0.19\text{ M}$  TfOH present. Bottom: CVs with  $\text{Mn}(\text{bpy})_2\text{Br}_2$ ,  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$ , or the remaining Mn material after crystallization under varied conditions. A scan rate of  $100\text{ mV/s}$  is used in all cases. The electrolyte is  $0.1\text{ M Bu}_4\text{NPF}_6$  in MeCN with glassy carbon working, platinum counter, and Ag-wire reference. The onset potentials in Table 1 are determined as shown by the purple arrow example on the middle graph.

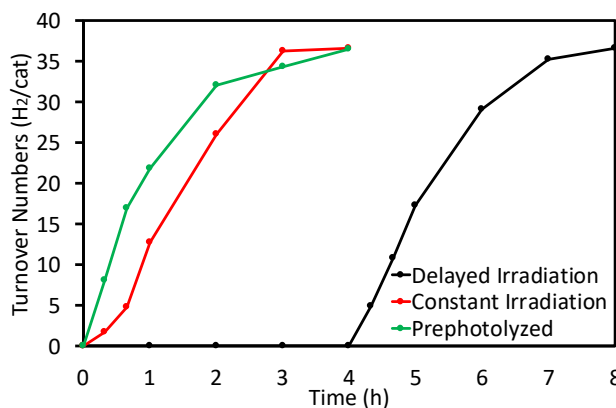
**Table 2.** Reactions performed with photolyzed  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  or  $\text{Mn}(\text{bpy})_2\text{Br}_2$ ,  $\text{FcMe}_{10}$  ( $33.7 \mu\text{mol}$ ), and  $0.19 \text{ M}$  TfOH (or replacement acid) in MeCN ( $5 \text{ mL}$ ) for 4 hours unless otherwise noted. TON vs. time plots are shown in Figures S17-22.

Entry	[catalyst]	Change	TON of $\text{H}_2$	TOF <sup>a</sup> ( $\text{hr}^{-1}$ )	$\text{H}_2$ yield <sup>b</sup>
<i>Benchmark Experiment and Controls</i>					
1	0.1 mM	none	29	81	85%
2	none	no catalyst	<1	<1	0%
3	none	no catalyst, +2% $\text{H}_2\text{O}$	<1	<1	0%
4	0.1 mM	no $\text{FcMe}_{10}$	<1	<1	0%
5	0.1 mM	no TfOH	<1	<1	0%
6	0.1 mM	– $\text{FcMe}_{10}$ , +BIH <sup>c</sup>	<1	<1	0%
7	0.1 mM	– $\text{FcMe}_{10}$ , +ferrocene	<1	<1	0%
<i>Acid Effects</i>					
8 <sup>d</sup>	0.1 mM	–TfOH, +[NC- <i>p</i> - $\text{C}_6\text{H}_4\text{NH}_3$ ] <sup>+</sup>	25	8	74%
9	0.1 mM	–TfOH, +TsOH	22	12	65%
10	$\text{Mn}(\text{bpy})_2\text{Br}_2$ (0.1 mM)	–TfOH, +TsOH	20	13	59%
11	0.1 mM	–TfOH, +TFA	<1	<1	0%
12	0.1 mM	–TfOH, +AcOH	<1	<1	0%
<i><math>\text{H}_2\text{O}</math> Effects</i>					
13	0.1 mM	+2% $\text{H}_2\text{O}$	34	24	quant.
14	0.1 mM	+5% $\text{H}_2\text{O}$	10	13	29%
15	0.1 mM	+10% $\text{H}_2\text{O}$	5	11	15%
<i>Catalyst Durability Evaluation</i>					
16	0.01 mM	+2% $\text{H}_2\text{O}$	340	140	quant.
17	1.0 $\mu\text{M}$	+2% $\text{H}_2\text{O}$	3400	1,600	quant.
18	0.1 $\mu\text{M}$	+2% $\text{H}_2\text{O}$	34,000	16,000	quant.
19	0.01 $\mu\text{M}$	+2% $\text{H}_2\text{O}$	340,000	120,000	quant.
20	1.0 nM	+2% $\text{H}_2\text{O}$	3,400,000	1,100,000	quant.
21 <sup>e</sup>	1.0 nM	+2% $\text{H}_2\text{O}$ , 3x $\text{FcMe}_{10}$	10,000,000	1,300,000	quant.
22 <sup>e</sup>	$\text{Mn}(\text{bpy})_2\text{Br}_2$ 1.0 nM	+2% $\text{H}_2\text{O}$ , 3x $\text{FcMe}_{10}$	10,000,000	1,300,000	quant.

<sup>a</sup> TOF is calculated as an initial rate by taking a sample after the first 20 minutes of the reaction and dividing the observed TON by the time elapsed. Note: the TOF value only establishes a lower limit for catalytic rate (see discussion below), and the TON value for  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  is calculated with respect to the amount of starting complex rather than the amount of active catalyst formed. <sup>b</sup> % yield of  $\text{H}_2$  is calculated based on the number of  $\text{H}_2$  molecules observed divided by half the number of  $\text{FcMe}_{10}$  molecules present and multiplied by 100%. <sup>c</sup> 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH) as a sacrificial reductant. <sup>d</sup> Reaction was monitored over 12 hours. <sup>e</sup> Reaction was monitored over 22 hours.



**Figure 4.** Charge passage over time graph for CPE experiments with  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  (black, 1 mM) and photolyzed  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  (red, 1 mM). The blue line is a background reaction with all components kept constant minus catalyst.



**Figure 5.** TON vs time under identical reaction conditions (0.1 mM catalyst, 0.19 M TfOH,  $33.7 \mu\text{mol}$   $\text{FcMe}_{10}$ , and 2%  $\text{H}_2\text{O}$ ), but with varying light exposure parameters. The black curve shows a reaction that was kept shielded from light for four hours prior to being placed in front a solar simulator at 1 sun intensity. The red curve shows a reaction that was irradiated constantly. The green curve shows a reaction that was pre-photolyzed before TfOH addition and then placed in the dark.

Upon exposure of  $\text{Mn}(\text{bpy})_2(\text{Br})_2$  to TfOH in the dark (bottom: red line) or in the light (bottom: black line) a current increase is observed ( $i_{\text{cat}}/i_p$  of 23 and 30, respectively) with a slight shoulder near the curve peak emerging which is not apparent from the curve with  $\text{Mn}(\text{bpy})_2(\text{Br})_2$  in the absence of TfOH (bottom: blue line) (Figure 3). No dramatic difference is observed in the light or dark when TfOH is present with respect to curve shape or current increase. The slight shoulder observed near -1.1 V and the reduction wave peak at -1.20 V of the  $\text{Mn}(\text{bpy})_2(\text{Br})_2$  match closely in potential to the two shoulder features observed when  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  is exposed to light and TfOH (bottom: green line). The features of the  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  voltammogram taken in the presence of light and TfOH (green line) appear to be comprised of the catalytic reduction wave features of the bipyridine free Mn material (gray line with TfOH, purple line without TfOH) and  $\text{Mn}(\text{bpy})_2\text{Br}_2$ .

To confirm the current enhancement observed via CV is due to proton reduction, controlled potential electrolysis (CPE) studies were carried out at the initial current plateau potential observed via CV for photolyzed  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  in the presence of TfOH with a glassy carbon working electrode, glassy carbon counter electrode, and a silver wire reference electrode. Molecular hydrogen is produced with a Faradaic efficiency (FE) of 100% when applying a constant potential at the first reduction (-0.80 V) of photolyzed  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  (Figure 4, red line). However, at the same potential negligible molecular hydrogen relative to the background reaction (blue line) is produced when  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  is kept in the dark (black line). A steady rate of charge passing is observed over a 2 hour time period for photolyzed  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  with no evidence of catalyst decomposition based on the lack of charge passage rate changes.

Thermal catalytic studies with an SED ( $\text{FcMe}_{10}$ ) were undertaken having found the resulting complex from irradiation of  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  to have desirable rates of proton reduction and favorable reaction energetics via electrochemical analysis. The use of a potential redox mediator as an SED is attractive in allowing for the probing of catalyst durability with an SED that could be rendered catalytic in EC/PEC systems.<sup>5-10</sup>  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  was first dissolved in MeCN and TfOH, then  $\text{FcMe}_{10}$  was added in the dark. After 4 hours, no appreciable  $\text{H}_2$  was detected in the headspace (Figure 5, black line). Upon exposure to 1 sun intensity solar simulated light for 5 minutes, catalysis immediately began, with no additional irradiation needed and catalysis proceeded until a high yield (85%) of  $\text{H}_2$  was observed with respect to the amount of  $\text{FcMe}_{10}$  added assuming 2  $\text{FcMe}_{10}$  SED molecules are required per  $\text{H}_2$  molecule produced (Table 2, entry 1). This corresponds to 29 turnover numbers (TONs) calculated via the equation  $\text{TON} = (\text{H}_2 \text{ moles}/\text{Mn-catalyst moles})$ . A turnover frequency (TOF) of  $81 \text{ hr}^{-1}$  is observed over the initial 20 minute period of the reaction, according to the equation  $\text{TOF} = \text{TON}/\text{time}$ . The reaction was found to follow a near identical profile with respect to a TON versus time plot during continuous irradiation (red line) or irradiation prior to acid and SED addition (green line) indicating the reaction is photoinitiated without any significant deactivation pathway, which would require photons to access the active catalyst again (i.e. continuous illumination is not necessary, Figure 5). Removal of the Mn catalyst,  $\text{FcMe}_{10}$ , or TfOH from the reaction mixture lead to no appreciable  $\text{H}_2$  formation (Table 2, entries 2-5; Figure S22). Exchange of the SED for either BIH or ferrocene led to no  $\text{H}_2$  product formation, presumably due to these SEDs being less reducing, resulting in endothermic reactions with free energies of +0.08 V and +0.18 V, respectively (Table 2, entries 6-7; Figure S22).<sup>12</sup>

Exchange of the TfOH proton source for acids with higher  $pK_a$ s was evaluated with 4-cyanoanilinium tetrafluoroborate, TsOH, trifluoroacetic acid (TFA), and acetic acid (AcOH) to examine the effects of changing the free energy of the reaction being catalyzed (Table 2, entries 8-12; Figure S20). The free energies for the proton reduction reactions with  $\text{FcMe}_{10}$  are estimated at -0.07 V, +0.03 V, +0.78 V, and +1.42 V for 4-cyanoanilinium tetrafluoroborate, TsOH, TFA, and AcOH, respectively. Notably, the rate of chemical reduction with 4-cyanoanilinium is slowed relative that of TfOH (TOF of 8 versus  $81 \text{ hr}^{-1}$ , respectively); however, the overall TON value is similar at 25 versus 29 for the reportedly more well-behaved 4-cyanoanilinium (Table 2, entry 8).<sup>31</sup> Interestingly, TsOH was found to be a competent proton source for this reaction, indicating the thermal energy present at room temperature is sufficient to overcome any activation energy barriers and drive this slightly endothermic reaction. A TON of 22 was observed for a 65%  $\text{H}_2$  yield with respect to the SED. A slower TOF is observed with TsOH and photolyzed  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  to TfOH (12 versus  $81 \text{ hr}^{-1}$ ). Similarly, crystallographically characterized  $\text{Mn}(\text{bpy})_2\text{Br}_2$  was found to react TsOH for 20 TONs and a TOF of up to  $13 \text{ hr}^{-1}$  (Table 2, entry 10; Figure S21). As expected, the larger endothermic reactions with TFA and AcOH gave no appreciable reactivity.

Water was explored as an additive for this reaction since  $\text{Mn}(\text{bpy})_3(\text{CO})_3\text{Br}$  is known to undergo dramatic catalysis changes in the presence of  $\text{H}_2\text{O}$ .<sup>23</sup> Addition of 2%  $\text{H}_2\text{O}$  v/v with MeCN led to an increase in observed  $\text{H}_2$  with a TON of 34 for a quantitative  $\text{H}_2$  yield (Table 2, entry 13; Figure S19). The TOF of the reaction slowed by  $\sim 4\times$  upon water addition for this reaction, although it is not clear if this is due to a change in  $pK_a$  of the proton source with the new solvent medium changing the reaction energetics or some other role. Further increasing the percent composition of  $\text{H}_2\text{O}$  to 5% and 10% lead to diminished TON values of 10 and 5 along with decreased percent yield values of  $\text{H}_2$  at 29% to 15% and a dramatic slowing of catalyst TOF by  $10\times$  (Table 2, entries 14 & 15, Figure S19). This loss in reactivity may be due to changes in reaction energetics or additional loss of solubility of  $\text{FcMe}_{10}$ , which is already sparingly soluble in pure MeCN and reacts into solution in dry MeCN over time. The solubility of  $\text{FcMe}_{10}$  is likely rate limiting under these conditions.

With optimal conditions identified for the proton reduction reaction, the catalyst durability was probed by decreasing the catalyst concentration and holding the remaining component concentrations constant (Table 2, entries 16-20; Figure S17). Interestingly, from 0.1 mM to 1.0 nM photolyzed  $\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  was found to quantitatively consume electrons from  $\text{FcMe}_{10}$  to produce  $\text{H}_2$  with up to 3,400,000 TONs observed with a TOF observed of  $>1,000,000 \text{ hr}^{-1}$ . Given that complete consumption of  $\text{FcMe}_{10}$  is turnover limiting, CPE was attempted with  $\text{FcMe}_{10}$  to probe if an increase in  $\text{H}_2$  generation rate electrochemically could be observed with an added SED that might have advantageous interfacial electron transfer kinetics at an electrode surface relative to the active catalyst; however, catalysis was found to slow during electrolysis when  $\text{FcMe}_{10}$  was added due to electrode fouling as a result of the limited solubility of  $\text{FcMe}_{10}$ . The near linear changes in TOF across the 5 orders of magnitude in catalyst concentrations probed in the thermal reaction suggests that the reaction rate is likely limited by the relative concentration of the electron source in solution under optimized conditions. The solubility limit of  $\text{FcMe}_{10}$  is estimated at 1 mg per 75 mL of MeCN, and solid  $\text{FcMe}_{10}$  can be observed reacting into solution over time. To assess the catalyst durability limits, a large excess of  $\text{FcMe}_{10}$  was added, and a TON value of  $\sim 10,000,000$  was

observed with a TOF value of 1,300,000 hr<sup>-1</sup> (Table 2, entry 21; Figure S18). The same values are observed with Mn(bpy)<sub>2</sub>Br<sub>2</sub> as the starting complex (Table 2, entry 22). The leveling off of TOF after dramatically increasing the amount of FcMe<sub>10</sub> while holding catalyst concentration constant further suggests the electron source solubility is limiting catalytic rates. Thus, the reported TOF values can only be used to establish a lower limit catalyst TOF under the optimized conditions since the maximum rate cannot be observed due to the limited solubility of FcMe<sub>10</sub>. Notably, the TOF and TON values in Table 2 can be effectively doubled when starting with Mn(bpy)(CO)<sub>3</sub>Br since Mn(bpy)<sub>2</sub>Br<sub>2</sub> is formed seemingly cleanly under the reaction conditions in >90% yield relative to bpy ligand and displays very similar reactivity.

## Conclusion

Mn(bpy)(CO)<sub>3</sub>Br was shown to photolyze to a new catalyst for H<sup>+</sup> reduction. Upon addition of H<sup>+</sup>, Mn(bpy)<sub>2</sub>(Br)<sub>2</sub> could be crystallized after photolysis of Mn(bpy)(CO)<sub>3</sub>Br, and upon subjecting these crystals to the reaction conditions, similar reactivity was observed to Mn(bpy)(CO)<sub>3</sub>Br in the same reaction conditions. The photogenerated catalyst was found to catalyze the reduction of protons at a lower potential and a larger  $i_{cat}/i_p$  ratio than Mn(bpy)(CO)<sub>3</sub>Br via cyclic voltammetry and controlled potential electrolysis. In a thermal reaction setup, the photoinduced species was found to be exceptionally durable with >10,000,000 TON observed and a fast catalysis TOF of 1,300,000 hr<sup>-1</sup> directly observed from the H<sub>2</sub> amount formed. Decomposition of the catalyst was not observed in these studies. This is a relatively rapid, durable catalytic system, which powers the low overpotential, thermal reaction of TsOH with FcMe<sub>10</sub> at about +0.03 eV. Future work is aimed at characterizing the intermediates involved in the process and integration of this catalyst into a full PEC/EC system for water splitting.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information containing experimental details, additional spectroscopic information, catalysis experiments, and crystallographic information is available as PDF and CIF files free of charge on the ACS Publications website.

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### Notes

The authors declare no conflicts of interest.

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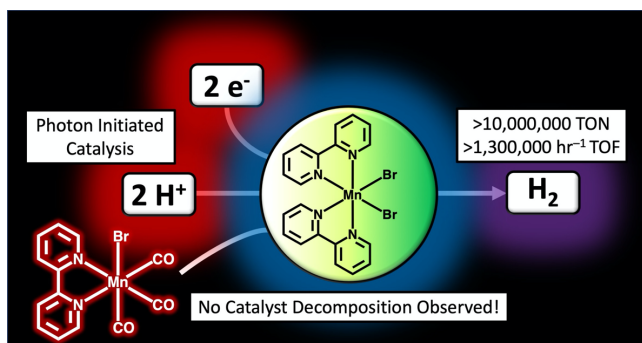
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## Table of Contents/Graphical Abstract Image



$\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$  is converted to  $\text{Mn}(\text{bpy})_2\text{Br}_2$  upon exposure to light and an acid source. This transformation was found to rapidly occur in situ and was confirmed by x-ray crystallography.  $\text{Mn}(\text{bpy})_2\text{Br}_2$  was found to promote the rapid chemical and electrochemical reduction of protons at a low driving force with high durability.

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