Supporting Information for

Electrochemical Generation of Hydrogen from Acetic Acid Using a Molecular Molybdenum-Oxo Catalyst

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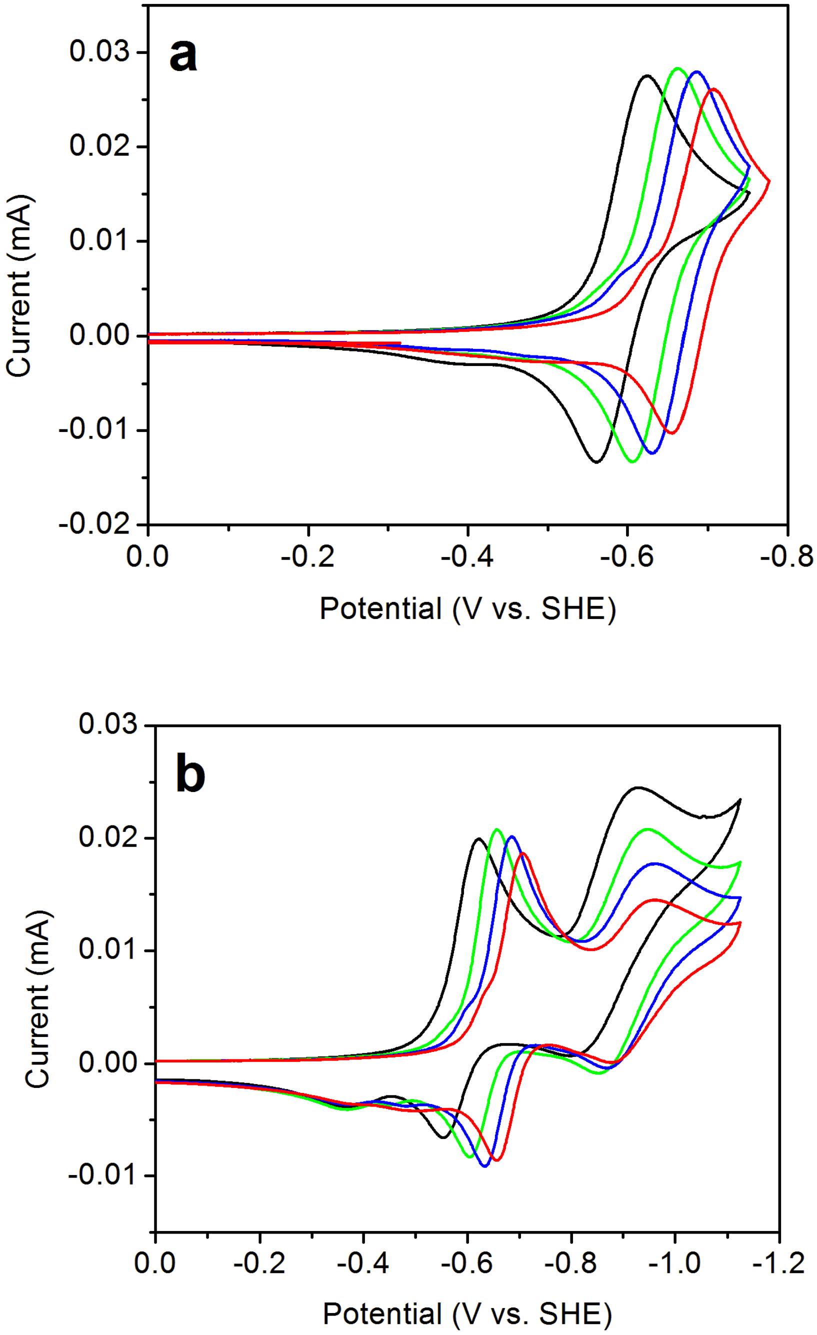

Figure S1. Cyclic voltammograms of the a) first and b) second reductions of 0.5 mM **1**$(CF_3SO_3)_2$ and 9 mM of benzoic acid in a 0.1 M of $(Bu_4N)PF_6$ acetonitrile solution with 0.9 mM (black, 10:1), 5 mM (green, 2:1), 7 mM (blue, 3:1), and 9 mM (red, 1:1) of tetrabutylammonium benzoate at a glassy carbon disc electrode and a scan rate of 0.1 V/s. Relative to a 1:1 ratio of benzoic acid to tetrabutylammonium benzoate, the first and second reduction events shift by 90 mV and 56 mV, respectively, in the presence of a 10:1 ratio of benzoic acid to tetrabutylammonium benzoate.

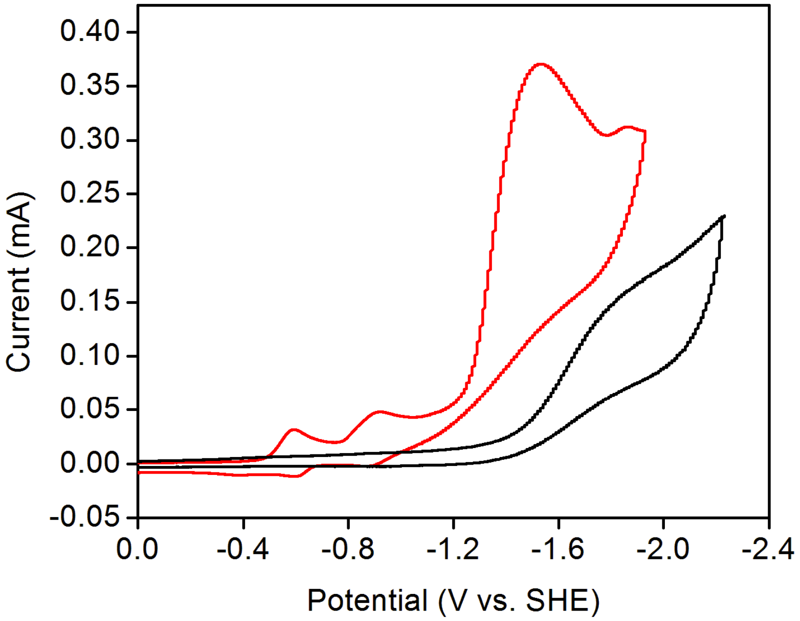

Figure S2. Cyclic voltammogram in the absence (black) and presence (red) of 0.7 mM **1**($(CF_3SO_3)_2$) in a 0.1 M of $(Bu_4N)PF_6$ acetonitrile solution with 35 mM of acetic acid at a glassy carbon disc electrode and a scan rate of 0.1 V/s.

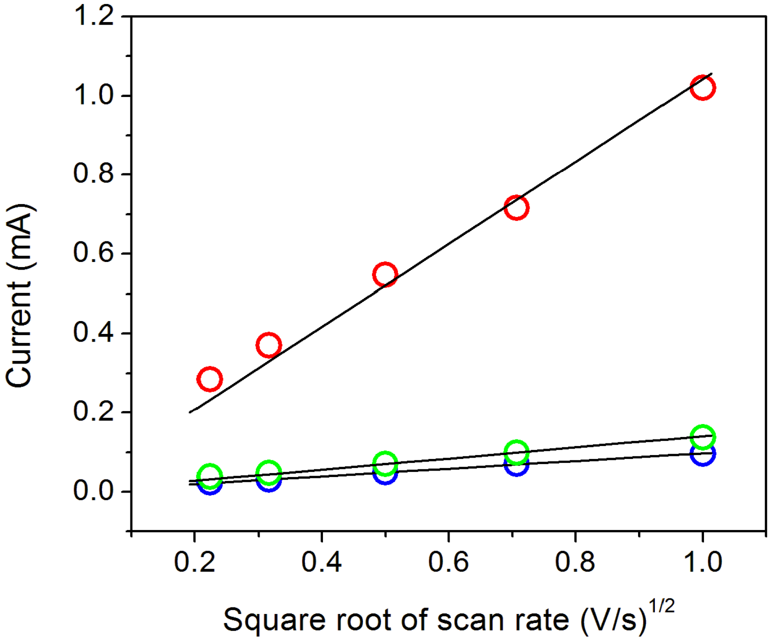

Figure S3. Plot of the current versus the square root of the scan rate for the two precatalytic anodic waves at $E_p = -0.64$ V (blue circles, $R^2 = 0.999$) and $E_p = -0.84$ V (green circles, $R^2 = 0.999$) and the catalytic reduction of protons at −1.6 V vs SHE (red circles, $R^2 = 0.998$) for 0.7 mM **1**$(CF_3SO_3)_2$ in a 0.1 M of $(Bu_4N)PF_6$ acetonitrile solution with 35 mM of acetic acid at a glassy carbon disc electrode for scan rates from 0.025 to 1 V/s. The linear fits to the data indicate that the reduced species are freely diffusing in solution at all potentials.

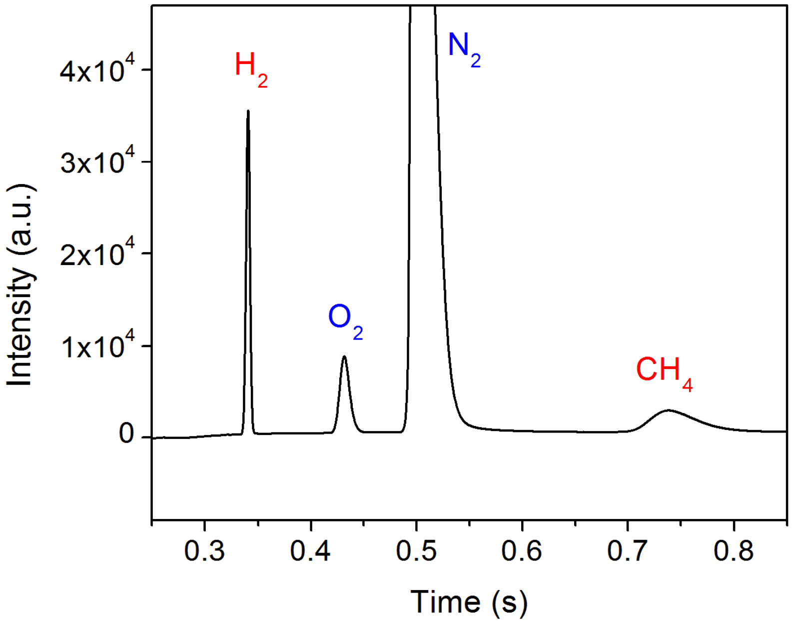

Figure S4. GC trace after a 1-h controlled-potential electrolysis at −1.6 V of 0.1 mM **1**(CF_3SO_3)$_2$ in a 0.1 M (Bu_4N)PF_6 acetonitrile solution with 17 mM of acetic acid. A standard of CH_4 was added for calibration purposes.

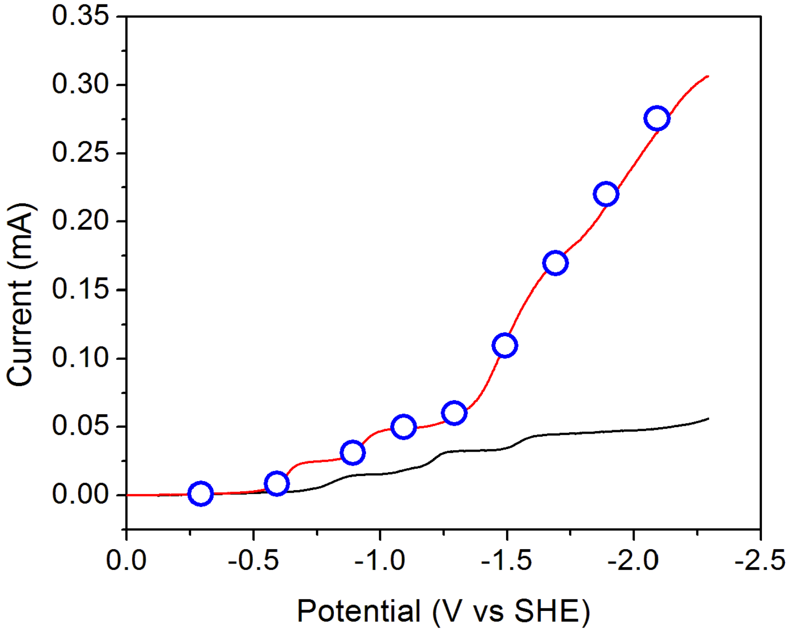

Figure S5. RDE voltammograms of 0.35 mM **1**(CF_3SO_3)$_2$ in the absence (black) and presence (red) of 5.2 mM of acetic acid in a 0.1 M of (Bu_4N)PF_6 acetonitrile solution. The blue circles are steady-state currents obtained from potential step chronoamperometry after $\tau = 2.5$ s.[1] Scan rate: 0.025 V/s, 400 rpm.

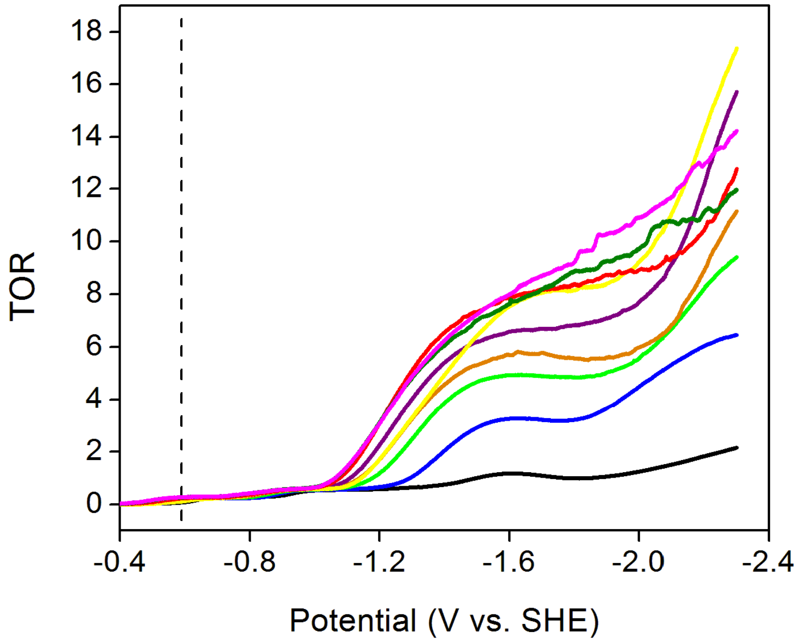

Figure S6. The apparent turnover rate, TOR, (see text for details), for 0.35 mM **1**$(CF_3SO_3)_2$ in a 0.1 M $(Bu_4N)PF_6$ acetonitrile solution in the presence of 5.2 mM (black), 17 mM (blue), 35 mM (green), 52 mM (orange), 70 mM (purple), 87 mM (yellow), 105 mM (red), 140 mM (olive), and 157 mM (magenta) of acetic acid, at a scan rate of 0.025 V/s and a rotation rate of 400 rpm, on a glassy carbon disc electrode. The dotted vertical line at −0.59 V vs. SHE indicates the thermodynamic potential for the reduction of acetic acid to H_2 in acetonitrile.[2]

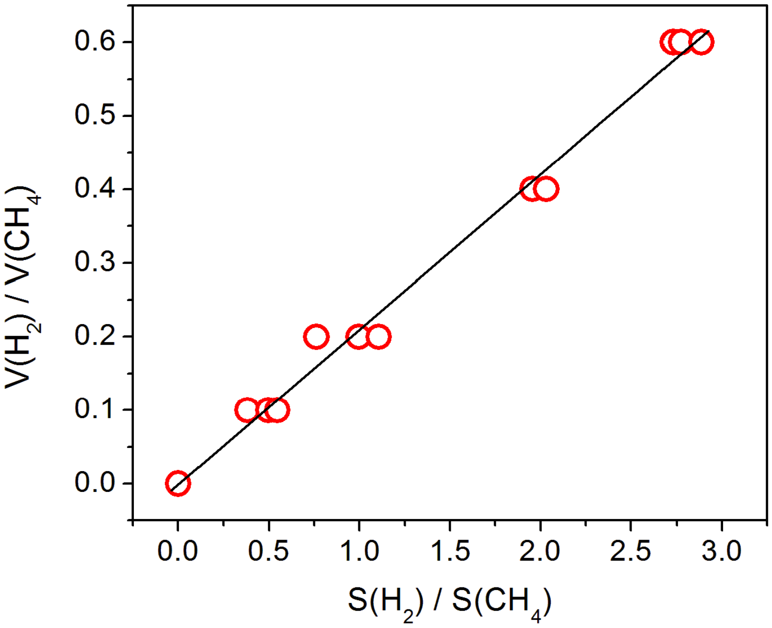

Figure S7. Calibration curve used for determining the Faradaic efficiency by **1**$(CF_3SO_3)_2$ for hydrogen production, where V is the volume of gas injected into the headspace and S is the integrated area of the peak signal in the gas chromatogram. The data was fitted to $y = 0.21x$, $R^2 = 0.9923$.

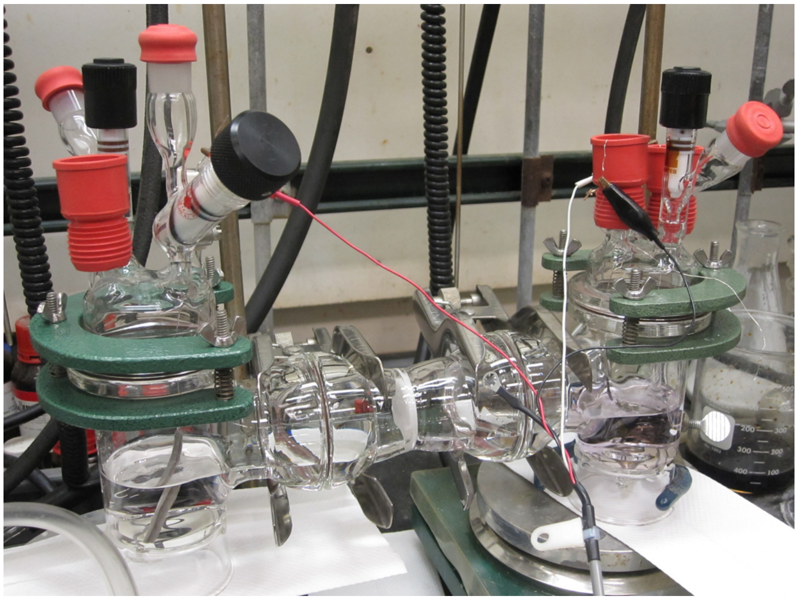

Figure 8. Photo of custom-made double compartment cell.

References

1) A. J. F. Bard and R. Larry R. Electrochemical Methods: Fundamentals and Applications; John Wiley & Sons: New York, **2001**.

2) V. Fourmond, P.-A. Jacques, M. Fontecave, and V. Artero. *Inorg. Chem.*, **2010**, *49*, 10338-10347.