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Supporting Information

## A 2,2'-Bipyridine-Containing Covalent Organic Framework Bearing Rhenium (I) Tricarbonyl Moieties for CO<sub>2</sub> Reduction

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 Table S1. Crystal data and structure refinement for 1.

C<sub>16</sub>H<sub>17</sub>CIN₅O₄Re

Formula weight	564.99		
Crystal system	monoclinic		
Space group	C <sub>2/c</sub>		
a (Å)	26.2689(18)		
b (Å)	8.5420(6)		
c (Å)	17.5006(12)		
α (°)	90		
β (°)	98.2270(10)		
γ (°)	90 3886.5(5)		
V (Å <sup>3</sup> )			
Z	8		
D <sub>calc</sub> (g/cm <sup>3</sup> )	1.931		
μ (Mo Kα) (mm <sup>-1</sup> )	6.422		
F (000)	2176		
Reflections collected	46175		
Independent reflections	5911 [R(int) = 0.0292]		
$R_1 (l > 2\sigma(l))$	0.0163		
wR <sub>2</sub> (all data)	0.0317		
Goodness-of-fit (GOF) on F <sup>2</sup>	1.029		

Table S2. Selected bond lengths (Å) for complex 1.

Bond	Bond length (Å)		
Re(1)-C(1)	1.899(18)		
Re(1)-C(2)	1.9252(16)		
Re(1)-C(3)	1.9249(18)		
Re(1)-Cl(1)	2.4848(4)		
Re(1)-N(1)	2.1755(13)		
Re(1)-N(2)	2.1707(13)		
C(1)-O(1)	1.144(2)		
C(2)-O(2)	1.150(2)		
C(3)-O(3)	1.151(2)		

**Table S3.** A comparison between select experimental (averaged) and calculated bond lengths for complex **1**. For  $\text{Re}(2,2'\text{-bpy})(\text{CO})_3\text{CI}$  the values are taken from previous reports[<sup>61</sup>]. Calculations were performed using the M06 functional with the 6-31G\* basis set for H, C, N, and O atoms and the LANL2DZ effective core potential and basis set for Cl and Re atoms.

	Experimental Bond Length (Å)		Calculated Bond Ler	ngth (Å)
Bond	Re(2,2'-bpy)(CO)₃CI 1		Re(2,2'-bpy)(CO)₃Cl	1
Re-N	2.175(7)	2.173(2)	2.203	2.204
Re-C(eq)	1.925(10)	1.925(3)	1.922	1.920
C-O (eq)	1.150(13)	1.151(3)	1.159	1.160



Figure S1. CO stretching region of the FTIR of a pressed pellet of 1 with KBr.

**Table S4.** Calculated carbonyl stretching mode frequencies from DFT calculations for  $Re(2,2'-bpy)(CO)_3CI$  and **1.** Calculations were performed using the M06 functional with the 6-31G\* basis set for H, C, N, and O atoms and the LANL2DZ effective core potential and basis set for CI and Re atoms.

Experimental Frequencies (cm <sup>-1</sup> )			Calculated Frequencies (cm <sup>-1</sup> )		
Carbonyl Stretching Mode <sup>[1]</sup>	Carbonyl Stretching Mode <sup>[1]</sup> Re(2,2'-bpy)(CO) <sub>3</sub> Cl <sup>16</sup>		Re(2,2'-bpy)(CO)₃Cl	1	
a' <sub>1</sub>	2025	2015	2129	2125	
a"	1918	1896 <sup>[2]</sup>	2050	2042	
a'2	1902		2030	2027	

[1] See visualization of carbonyl stretching modes in Figure S1. [2] Stretching modes a" and  $a'_2$  appear coalesced in Figure 2.



**Figure S2.** Visualization of the three characteristic carbonyl stretching modes in  $\text{Re}(2,2'-\text{bpy})(\text{CO})_3\text{CI}$  with pink vectors indicating nuclear motion. The character of the three carbonyl modes in **1** are identical to these.



**Figure S3.** Cyclic voltammograms of 0.5 mM complex **1** in an MeCN solution containing 0.1 M  $[nBu_4N][PF_6]$  under an atmosphere of N<sub>2</sub> at scan rates ranging from 100 to 1000 mV/s.



**Figure S4.** Plot showing the peak cathodic current density at -2.11 V (left) and -2.47 V (right) vs. Fc<sup>+/0</sup> as a function of the square root of the scan rate. The cathodic peak current density was obtained from the

cyclic voltammetry data of **1** (0.5 mM) in an MeCN solution containing 0.1 M [ $nBu_4N$ ][PF<sub>6</sub>] under an atmosphere of N<sub>2</sub>. The cathodic peak current density increases linearly with the square root of the scan rate indicative of a freely-diffusing species obeying the Randles-Sevcik equation.



**Figure S5.** Controlled potential electrolysis of **1** under N<sub>2</sub> (black) and under CO<sub>2</sub> (red). Conditions: **1** (0.5 mM) in 0.1 M solution of [ $nBu_4N$ ][PF<sub>6</sub>] in MeCN, measure at a potential of –2.57 V vs. Fc<sup>+/0</sup>.



**Figure S6**. FTIR spectra of a solution of **1** before (blue) and after (light-brown) CPE studies. Conditions used: **1** (0.5 mM) in MeCN solution containing 0.1 M [ $nBu_4N$ ][PF<sub>6</sub>] under an atmosphere of CO<sub>2</sub> at –2.57 V versus Fc<sup>+/0</sup>.

**Table S5.** CPE results for Complex **1**. Overall TON is calculated as  $mol_{CO}/mol_{catalyst}$ . TOF<sub>CPE</sub> (s<sup>-1</sup>) is calculated as described previously. TON<sub>CPE</sub> is calculated by multiplying TOF<sub>CPE</sub>(s<sup>-1</sup>) with the time for CPE studies (3600 s) (see "**TOF<sub>CPE</sub>** calculations from controlled potential electrolysis" section below for details).

Time, min	Charge (C)	Faradaic Efficiency, %	Overall	TOF <sub>CPE</sub>	TON <sub>CPE</sub>
			TON		
60	9.200	99	2	28	100,800

**Table S6.** Reduction potentials for a selection of rhenium tricarbonyl complexes bearing various 2,2'-bpy ligands.<sup>1</sup> The reduction potentials for complex **1** are from this study and the rest are from reference 1. The literature values were reported relative to the saturated calomel electrode (SCE). For the purpose of comparison, these values were converted to the Fe<sup>3+/2+</sup> couple in ferrocene by adding a value of –0.400 V to the reported potential.

Complex	1 <sup>st</sup> reduction potential (V vs. Fc <sup>+/0</sup> )	2 <sup>nd</sup> reduction potential (V vs Fc <sup>+/0</sup> )	Reference
Re(2,2'-bpy)(4,4'-COOH)(CO) <sub>3</sub> Cl	-1.34	-2.13	
Re(2,2'-bpy)(CO) <sub>3</sub> Cl	-1.74	-2.13	
Re(2,2'-bpy)(4,4'-Me)(CO) <sub>3</sub> Cl	-1.83	-2.17	1
Re(2,2'-bpy)(4,4'- <i>t</i> Bu)(CO) <sub>3</sub> Cl	-1.85	-2.23	
Re(2,2'-bpy)(4,4'-OMe)(CO) <sub>3</sub> Cl	-1.89	-2.26	
1	-2.11	-2.47	This work



**Figure S7**. Cyclic voltammograms of **1** (0.5 mM) in an MeCN solution containing 0.1 M [ $nBu_4N$ ][PF<sub>6</sub>] under an atmosphere of N<sub>2</sub> at varying concentrations of  $nBu_4NCI$  (TBACI).



**Figure S8**. Overlay of cyclic voltammetry data of **1** and  $\mathbf{1}^{OTf}$  (0.5 mM concentration each) in MeCN solutions containing 0.1 M [*n*Bu<sub>4</sub>N][PF<sub>6</sub>] under an atmosphere of N<sub>2</sub>.



**Figure S9.** Cyclic voltammogram scan rate dependence of  $\mathbf{1}^{OTf}$  (0.5 mM), in an MeCN solution containing 0.1 M [nBu<sub>4</sub>N][PF<sub>6</sub>] under an atmosphere of N<sub>2</sub>. Scan rates vary from 100 to 1000 mV/s.



**Figure S10.** Cyclic voltammogram scan rate dependence of 0.5 mM Zn(2,2'-bpy-5,5'diamine)(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O complex in an MeCN solution containing 0.1 M [nBu<sub>4</sub>N][PF<sub>6</sub>] under an atmosphere of N<sub>2</sub>. Scan rates vary from 100 to 1000 mV/s.



**Figure S11**. Molecular orbital diagrams and frontier orbital images for Re(2,2'-bpy)(CO)<sub>3</sub>Cl (HOMO-2, HOMO-3; blue) and **1** (HOMO-2', HOMO-3'; red). Calculations were performed using the M06 functional with the 6-311G\* basis set for H, C, N, and O atoms and the LANL2DZ effective core potential and basis set for Cl and Re atoms.



**Figure S12.** Overlay of the FTIR spectra of COF-2,2'-bpy-Re that displays 29.38 wt % Re incorporation (purple) and of COF-2,2'-bpy (red).



**Figure S13.** FTIR of  $Re(CO)_5CI$  in the CO stretching region.



**Figure S14.** HR XPS analysis of COF-2,2'-bpy-Re that displays 15.39 wt % Re: (a) N 1s core level XPS spectrum; (b) Cl 2p core level XPS spectrum; (c) Re 4f core level XPS spectrum.



**Figure S15.** HR XPS analysis of the rhenium precursor, Re(CO)<sub>5</sub>CI: (a) CI 2p core level XPS spectrum; (b) Re 4f core level XPS spectrum.



**Figure S16.** Controlled potential electrolysis of **2** in an atmosphere of CO<sub>2</sub> (red) and N<sub>2</sub> (black); conditions: 0.1 M [ $nBu_4N$ ][PF<sub>6</sub>] in MeCN, measured at a potential of –2.8 V vs. Fc<sup>+/0</sup>.

Time, min	Volume (CO), mL	Charge passed, coulombs	Faradaic Efficiency, %	Total TON
30	0.376	3.746	81	51
60	0.377	5.267	57	51

Table S7. Electrochemical data fo	r <b>2</b> .
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**Figure S17.** (a) Polarization curves of the composites based on COF-2,2'-bpy (purple), rhenium precursor,  $\text{Re}(\text{CO})_5\text{CI}$  (blue), carbon black and polyvinylidene fluoride (PVDF) by themselves (black), and **2** (red) under CO<sub>2</sub>; conditions: 0.1 M [*n*Bu<sub>4</sub>N][PF<sub>6</sub>] in MeCN, scan rate = 10 mV/s. (b) Controlled potential electrolysis of the composites based on COF-2,2'-bpy (purple), rhenium precursor (blue), carbon black and PVDF by themselves (black), and **2** (red) under CO<sub>2</sub>; conditions: 0.1 M [*n*Bu<sub>4</sub>N][PF<sub>6</sub>] in MeCN, scan rate = 10 mV/s. (b) Controlled potential electrolysis of the composites based on COF-2,2'-bpy (purple), rhenium precursor (blue), carbon black and PVDF by themselves (black), and **2** (red) under CO<sub>2</sub>; conditions: 0.1 M [*n*Bu<sub>4</sub>N][PF<sub>6</sub>] in MeCN, measured at a potential of –2.8 V vs. Fc<sup>+/0</sup>.



**Figure S18.** Polarization curve of **2** before catalysis (red) and after catalysis (black); conditions: 0.1 M  $[nBu_4N][PF_6]$  in MeCN, scan rate = 10 mV/s.



**Figure S19.** (a) Polarization curves of the postcatalysis solution (solution after CPE) measured with a clean glassy carbon electrode (black) and **2** (red) under of CO<sub>2</sub>; conditions: 0.1 M [ $nBu_4N$ ][PF<sub>6</sub>] in MeCN, scan rate = 10 mV/s. (b) Controlled potential electrolysis of the postcatalysis solution (solution after CPE) measured with a clean glassy carbon electrode (black) and **2** (red) under CO<sub>2</sub>; conditions: 0.1 M [ $nBu_4N$ ][PF<sub>6</sub>] in MeCN, measured at a potential of –2.8 V vs. Fc<sup>+/0</sup>.



**Figure S20.** HR XPS analysis of **2** after a 1 h electrolysis experiment in 0.1 M [ $nBu_4N$ ][PF<sub>6</sub>] acetonitrile solution at -2.8 V vs Fc<sup>0/+</sup>: (a) N 1s core level XPS spectrum; (b) Cl 2p core level XPS spectrum; (c) Re 4f core level XPS spectrum.



**Figure S21**. Cyclic voltammograms data  $(1^{st}, 2^{nd}, and 3^{rd} scans)$  of **1** (0.5 mM) in an MeCN solution containing 0.1 M [*n*Bu<sub>4</sub>N][PF<sub>6</sub>] under an atmosphere of N<sub>2</sub>.



**Figure S22**. Cyclic voltammogram data of **1** (0.5 mM) in MeCN solution containing 0.1 M [ $nBu_4N$ ][PF<sub>6</sub>] under an atmosphere of N<sub>2</sub>. Black curve: scan reversed after second reduction, red curve: scan reversed after first reduction.

TOF<sub>CPE</sub> calculations from controlled potential electrolysis.<sup>2</sup>

Equation (1) was used to determine TOF from CPE data, as previously reported.<sup>3,4</sup> This equation assumes that electron transfer to the catalyst is fast, obeying the Nernst law. In eq 1, *i* is the stable current transferred during CPE (*i* = charge\*FE/time, C/s), F is Faraday's constant (F = 96 485 C/mol), A is the surface area of the working electrode (A = 3 cm<sup>2</sup> for CPE),  $k_{cat}$  is the overall rate constant of the catalytic reaction, D is the diffusion coefficient (~1 × 10<sup>-5</sup> cm<sup>2</sup>/s), [cat] is the concentration of the catalyst without substrate ([cat] = 0.5 mM = 5 × 10<sup>-7</sup> mol/cm<sup>3</sup>). The value of D = ~ 1 × 10<sup>-5</sup> cm<sup>2</sup>/s was chosen based on the previous assessment of D for Re(2,2'-bpy)(4,4'-*tBu*)(CO)<sub>3</sub>Cl and Mn(2,2'-bpy)(4,4'-*tBu*)(CO)<sub>3</sub>Br which was found to be 1.1 × 10<sup>-5</sup> cm<sup>2</sup>/s (*Inorg. Chem.*, **2010**, *49* (20), 9283–9289; *Inorg. Chem.*, **2013**, *52*, 2484–2491).

$$TOF = k_{cat} = \frac{i^2}{F^2 A^2 D cat^2} \tag{1}$$

Controlled potential electrolysis (CPE) experiments, on the other hand, are bulk experiments that are run for prolonged periods of time and under constant stirring, and therefore, replenishing of the catalyst in the diffusion layer (at the electrode-liquid interface). In these experiments, the rate is limited by catalyst, substrate, reagents and products (catalyst, CO<sub>2</sub>, TFE, CO) diffusion to and away from the electrode. These experiments provide information about the stability and selectivity of the catalyst and selectivity of the catalyst, but do not provide any kinetic information intrinsic to the catalyst."

Using this equation, we obtained  $TON_{CPE}$  = 108,000, which is larger that 4, and therefore is adequate to establish catalysis.

## References

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