### **Supporting Information**

## Beyond scaling relations in electrocatalysis: unifying concepts from molecular systems and metallic surfaces

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## S1. Calculation of the effective overpotential $(\eta_{eff})$ for CO<sub>2</sub> reduction catalysts

#### S1.1. Calculating $\eta_{eff}$ for electrocatalysts with water as proton donor

The effective overpotential ( $\eta_{eff}$ ) was calculated for a large assembly of CO<sub>2</sub>-to-CO reduction catalysts.  $\eta_{eff}$  is calculated as in eq. 1 as the difference between the equilibrium potential ( $E_{eq}$ ) and the catalytic half-wave potential ( $E_{cat/2}$ ) for each catalyst. In the main text,  $E_{eq}$  is referred to as  $E_{CO_2/CO}$ :

$$\eta_{eff} = E_{eq} - E_{cat/2} \tag{1}$$

 $E_{eq}$  was calculated using the equations reported by Matsubara<sup>1</sup> which consider several reaction parameters including the nature of the proton donor used in the CO<sub>2</sub>RR and its ability to undergo homoconjugation. The equilibrium potentials ( $E_{eq,1}$ ) for the conversion of CO<sub>2</sub> to CO were calculated using eq. 3 for catalysts tested in the presence of a proton donor that does not undergo homoconjugation (for example, H<sub>2</sub>O, eq. 2):

$$3CO_{2(g)} + H_2O_{(sol,x)} + 2e^- \rightleftharpoons CO_{(g)} + 2HCO_{3(sol)}^- \qquad E_1^\circ \qquad (2)$$

$$E_{eq,1} \approx E_1^{\circ} + \frac{RT}{2F} \ln \left[ \frac{27}{4r^3} \frac{c_{eq,CO}}{(c_{cat}^*)^3} \frac{D_{CO}(D_{HCO_3^*})^2}{(D_{cat}D_{CO_2})^{\frac{3}{2}}} \right]$$
(3)

Where  $E_1^{\circ}$  (referred to as  $E_{CO_2/CO}^{0}$  in the main text) is the standard electrode potential for eq. 2 (given by eq. 4 below), *R*, *T*, and *F* are the gas constant, temperature, and Faraday's constant, respectively, *r* is the ratio of the diffusion-convection layer thickness (given by eq. 10 in section S1.3),  $c_{eq,CO}$  is the molar equilibrium concentration of CO (derived in section S1.4),  $c_{cat}^{*}$  is the molar concentration of the tested catalyst in the electrochemical setup (1 mM for all catalysts included in this study), and  $D_{CO}$ ,  $D_{HCO_3^-}$ ,  $D_{cat}$ ,  $D_{CO_2}$  are the diffusion coefficients for CO ( $D_{CO} = 2.2 \cdot 10^{-5} cm^2/s$ ),<sup>2</sup> HCO<sub>3</sub><sup>-</sup> ( $D_{HCO_3^-} = 1.0 * 10^{-5} cm^2/s$ ),<sup>3</sup> the catalyst, and CO<sub>2</sub>, respectively.  $D_{cat}$  and  $D_{CO_2}$  are given by eq. 11 and 12 as outlined in section S1.5.

 $E_1^\circ$  is calculated (vs SHE) based on the unified pH scale<sup>1,4</sup> as in eq. 4:

$$E_{1}^{\circ} = -\frac{1}{2F} \Big[ \Delta_{f} G^{\circ} (CO_{(g)}) + \Delta_{f} G^{\circ} (H_{2}O_{(l)}) + \Delta_{tr}^{l \to sol} G^{\circ} (H_{2}O) - \Delta_{f} G^{\circ} (CO_{2(g)}) + 2RT (\ln 10) p K_{a,abs}^{H_{2}O} (CO_{2(g)} + H_{2}O_{(sol,x)}) \Big]$$
(4)

Where  $\Delta_f G^{\circ}(CO_{(g)})$  and  $\Delta_f G^{\circ}(CO_{2(g)})$  are the standard formation Gibbs energy changes of CO and CO<sub>2</sub> in the gas phase with values of -137.163 kJ mol<sup>-1</sup> and -394.389 kJ mol<sup>-1</sup>, respectively.  $\Delta_f G^{\circ}(H_2O_{(l)})$  is the standard formation Gibbs energy change for H<sub>2</sub>O in the liquid state and has the value -237.178 kJ mol<sup>-1</sup>.  $\Delta_{tr}^{l \rightarrow sol} G^{\circ}(H_2O)$  is the standard Gibbs energy change for the transfer of H<sub>2</sub>O from pure liquid to a solvent-water mixture and was reported by Matsubara<sup>1</sup> to obtain the values of 0.67 kJ mol<sup>-1</sup> for dry *N*,*N*'-dimethylformamide (DMF) and 5.4 kJ mol<sup>-1</sup> for dry acetonitrile (MeCN).  $pK_{a,abs}^{H_2O}$  is the absolute apparent acid

dissociation constant on the unified pH scale for the reaction between CO<sub>2</sub> and H<sub>2</sub>O to form H<sup>+</sup> and bicarbonate (eq. 5). For water as proton donor in DMF or MeCN,  $pK_{a,abs}^{H_2O}$  was equal to 18.33 or 16.80, respectively.<sup>1</sup>

$$CO_{2(g)} + H_2O_{(sol,x)} \rightleftharpoons H^+_{(sol)} + HCO^-_{3(sol)}$$

$$\tag{5}$$

#### S1.2. Calculating $\eta_{eff}$ for electrocatalysts with phenol as proton donor

When the catalyst in question was tested in the presence of a proton donor (AH) capable of undergoing homoconjugation (for example, PhOH), the conversion of CO<sub>2</sub> to CO is represented by the reactions in eq. 6 and 7, and the equilibrium potential ( $E_{eq.2}$ ) is given by eq. 8:

$$CO_{2(g)} + 2AH_{(sol)} + 2e^{-} \rightleftharpoons CO_{(g)} + 2A_{(sol)}^{-} + H_2O_{(sol,x)} \quad E_2^{\circ} \quad (6)$$

$$CO_{2(g)} + 4AH_{(sol)} + 2e^{-} \rightleftharpoons CO_{(g)} + 2AHA_{(sol)}^{-} + H_2O_{(sol,x)} \quad (7)$$

$$E_{eq,2} \approx E_2^{\circ} + \frac{RT}{F} \ln K_{homo} + \frac{RT}{2F} \ln \left[ \frac{8}{r^3} \frac{c_{eq,CO}(c_{AH}^{*})^2}{(c_{cat}^{*})^3} \frac{D_{CO}(D_{AHA}^{-})^2}{((D_{cat})^3(D_{AH})^2 D_{CO_2})^{\frac{1}{2}}} (c_{AH}^{*})^2 \right] \quad (8)$$

Where  $E_2^{\circ}$  is the standard electrode potential for eq. 6 (given by eq. 9 below),  $K_{homo}$  is the homoconjugation formation constant (equal to  $10^{4.4}$  for PhOH),  $c_{AH}^{*}$  is the molar concentration of the proton donor in the electrochemical setup, and  $D_{AH}$  and  $D_{AHA^-}$  are the diffusion coefficients for the proton donor and its homoconjugate, respectively. For PhOH, these have values of  $D_{AH} = 1.1 * 10^{-5} cm^2/s$  and  $D_{AHA^-} = 7.26 * 10^{-6} cm^2/s$ .<sup>1</sup>

 $E_2^{\circ}$  was calculated in the same way as  $E_1^{\circ}$  but using the absolute apparent acid dissociation constant for the acid (PhOH) instead of H<sub>2</sub>O + CO<sub>2</sub> (eq. 9).  $pK_{a,abs}^{H_2O}(PhOH)$  has a value of 22.75 in DMF and 21.0 in MeCN.<sup>1</sup>

$$E_{2}^{\circ} = -\frac{1}{2F} \Big[ \Delta_{f} G^{\circ} (CO_{(g)}) + \Delta_{f} G^{\circ} (H_{2}O_{(l)}) + \Delta_{tr}^{l \to sol} G^{\circ} (H_{2}O) - \Delta_{f} G^{\circ} (CO_{2(g)}) + 2RT (\ln 10) p K_{a,abs}^{H_{2}O} (PhOH) \Big]$$
(9)

#### S1.3. Calculation of the ratio of the diffusion-convection layer thickness, r

The ratio of the diffusion-convection layer thickness, r, was calculated from eq. 10 below where  $\delta$  is the diffusion-convection layer thickness assumed to equal 50 µm and  $TOF_{\text{max}}$  is the maximum turnover frequency for the catalyst in question:

$$r = \frac{\delta}{\sqrt{\frac{D_{CO_2}}{TOF_{max}}}} \tag{10}$$

This equation was derived on the basis of the calculations presented in the work by Matsubara.<sup>1</sup>

#### **S1.4. Derivation of** *c*<sub>eq,CO</sub>

The equilibrium concentration of CO,  $c_{eq,CO}$ , was determined via interpolation using two points of  $c_{eq,CO}$  at different  $x_{H_2O}$  (vol% of water in the system). A linear correlation is assumed to exist between  $\ln(c_{eq,CO})$  and  $x_{H_2O}$ , so  $c_{eq,CO}$  can be determined by knowing  $x_{H_2O}$  of the system. In DMF,  $c_{eq,CO}$  was assumed to equal 0.954 mM for  $x_{H_2O} = 1$  (i.e. in pure water, reference<sup>2</sup>) and 2.5 mM for  $x_{H_2O} = 0.5$  In MeCN,  $c_{eq,CO}$  was assumed to equal 0.954 mM for  $x_{H_2O} = 1$  (reference <sup>2</sup>) and 9.06 mM for  $x_{H_2O} = 0$  (reference<sup>6</sup>). Using these constants, the plot in Figure S1 could be constructed and used to determine  $c_{eq,CO}$  for each catalytic system.



**Figure S1.**  $\ln(c_{eq,CO})$  as a function of  $x_{H_2O}$  based on the interpolation of two points.

#### S1.5. Determination of $D_{cat}$ and $D_{CO_2}$

 $D_{cat}$  and  $D_{CO_2}$  were estimated using the Stokes-Einstein-Sutherland relations to give eq. 11 and 12:

$$D_{cat} = D_{cat,0} \cdot \frac{\eta_1}{\eta_2} \tag{11}$$

$$D_{CO_2} = D_{CO_2,0} \cdot \frac{\eta_{1'}}{\eta_{2'}} \tag{12}$$

Where  $D_{cat,0}$  is assumed to have a value of  $0.5 \cdot 10^{-5} cm^2/s$  in water  $(x_{H_20} = 1)$  for manganese and rhenium bipyridine complexes, and a value of  $0.83 \cdot 10^{-6} cm^2/s$  for iron porphyrins in DMF  $(x_{H_20} = 0.001)$ .<sup>1</sup>  $D_{CO_2,0}$  has a value of  $2.0 \cdot 10^{-5} cm^2/s$  in water.<sup>3</sup>  $\eta_1$  and  $\eta_1$ , are the viscosities of the solvent-water mixtures under the conditions of  $D_{cat,0}$  and  $D_{CO_2,0}$ , respectively.  $\eta_2$  and  $\eta_2$ , are the viscosities of the solvent-water mixtures at the specific  $x_{H_20}$  used for the catalyst in question. The viscosities are given by eq. 13 and 14 for a MeCN-water mixture and a DMF-water mixture, respectively:<sup>1,7</sup>

$$\eta \left[ cP \right] = -1.2822x^3 + 2.1372x^2 - 0.3016x + 0.3469 \quad \text{for } 0 \le x = x_{H_20} \le 1 \tag{13}$$

$$\begin{aligned} \eta \left[ cP \right] &= 11.349x^6 + 13.643x^5 - 93.32x^4 + 95.625x^3 - 31.91x^2 + 4.7261x + 0.8046 \\ \text{for} \quad 0 \leq x = x_{H_2O} \leq 1 \end{aligned}$$

#### S1.6. Justification for the use of Ecat/2

The effective overpotential is defined as the difference between the potential required for catalysis ( $E_{cat}$ ) and the thermodynamic potential of the catalyzed reaction ( $E_{rxn}$ ).<sup>8,9</sup> Two primary strategies have been employed to estimate the value of  $E_{cat}$ : (1) using the standard potential of the catalyst's redox couple that initiates catalysis ( $E_{1/2}$ ) and (2) using the potential at which half of the maximum catalytic current is observed ( $E_{cat/2}$ ).

In the specific case of FeTPP catalysts, the standard potential of the redox couple initiating catalysis (Fe<sup>1/0</sup> for CO<sub>2</sub>RR) is essentially equal to  $E_{cat/2}$ .<sup>10</sup> This equivalence justifies the interchangeable use of  $E_{cat/2}$  and  $E_{1/2}$  in these cases.

In other cases, the relationship between  $E_{cat/2}$  and  $E_{1/2}$  depends on the reaction mechanism. However, as shown in the same work by Costentin and Savéant,<sup>10</sup> for EC', ECCE, or ECEC mechanisms when the same substrate is involved in both chemical steps, the potential difference between  $E_{cat/2}$  and  $E_{1/2}$  remains constant, even when the concentration or identity of the reactants and products changes. Consequently, the slopes of the identified scaling relationships should remain unchanged, regardless of whether  $E_{cat/2}$  or  $E_{1/2}$  is used. Our analysis assumes this assumption holds in all studied cases.

Additionally, as noted by Appel and Helm,<sup>11</sup> when side phenomena prevent the observation of a well-defined S-shaped catalytic wave, determining an accurate  $E_{cat/2}$  can be challenging. However, even in non-ideal catalytic waves, the variance in the determined  $E_{cat/2}$  value remains minimal when it is determined as the potential at half of the maximum catalytic current.

#### S2. Compilation of catalyst data extracted from literature, reaction conditions, and calculated effective overpotentials

**Table S1.** Overview of key metrics used in the calculation of  $\eta_{eff}$  for each catalyst included in this study. Electrode potentials were converted to Fc/Fc<sup>+</sup> by subtracting 694 mV from potentials recorded vs SHE or NHE in DMF.<sup>12,13</sup> In MeCN, potentials were converted from SHE to Fc/Fc<sup>+</sup> by subtracting 624 mV.<sup>14</sup>

Cata-	E <sub>cat/2</sub>	Ref.	log(TOF <sub>max</sub> )	Conditions (sol-	$x_{H_20}$	r	Ceq,CO	$D_{cat}  imes$	<b>D</b> <sub>CO2</sub> ×	$E_1^\circ$ [V vs	$E_2^\circ$ [V vs	E <sub>eq</sub> [V vs	$\eta_{eff}$ [V]
lyst	[V vs	elec-		<pre>vent + acid(s))</pre>	(vol%)		[mM]	107	10 <sup>5</sup>	Fc/Fc <sup>+</sup> ]	Fc/Fc <sup>+</sup> ]	Fc/Fc <sup>+</sup> ]	
	ref.]	trode						[cm <sup>2</sup> /s]	[cm <sup>2</sup> /s]				
						1.47							
Fe1 <sup>13</sup>	-1.42	NHE	4.10	$DMF + 5.5 M H_2O$	0.321	$\times 10^2$	1.84	5.31	1.45	-1.89	-	-1.72	0.394
				DMF + 0.1 M		2.73							
Fe1 <sup>15</sup>	-2.15	Fc/Fc+	2.83	PhOH	0.001	$\times 10^{1}$	2.50	8.31	2.27	-	-2.15	-1.87	0.277
				$DMF + 0.1 M H_2O$		6.75							
Fe1 <sup>16</sup>	-1.43	SHE	3.60	+ 0.1 M PhOH	0.008	$\times 10^{1}$	2.48	8.00	2.19	-1.89	-	-1.70	0.420
				DMF + 0.1 M H2O		3.19							
Fe1 <sup>16</sup>	-1.43	SHE	4.95	+ 1.0 M PhOH	0.008	$\times 10^2$	2.48	8.00	2.19	-1.89	-	-1.76	0.360
				$DMF + 0.1 M H_2O$		1.90							
Fe1 <sup>16</sup>	-1.43	SHE	4.50	+ 3.0 M PhOH	0.008	$\times 10^2$	2.48	8.00	2.19	-1.89	-	-1.74	0.380
				DMF + 0.1 M		4.50							
Fe1 <sup>12</sup>	-1.43	SHE	3.26	PhOH	0.001	$\times 10^{1}$	2.50	8.31	2.27	-	-2.15	-1.89	0.229
				DMF + 0.75 M		1.28							
Fe1 <sup>12</sup>	-1.43	SHE	4.17	PhOH	0.001	$\times 10^2$	2.50	8.31	2.27	-	-2.15	-1.83	0.293
				DMF + 3.0 M		3.38							
Fe1 <sup>12</sup>	-1.43	SHE	5.01	PhOH	0.001	$\times 10^2$	2.50	8.31	2.27	-	-2.15	-1.80	0.326
						3.12							
Fe1 <sup>17</sup>	-1.43	NHE	4.75	DMF/H <sub>2</sub> O 9:1	0.323	$\times 10^2$	1.83	5.29	1.45	-1.89	-	-1.75	0.375
10						2.14							
Fe2 <sup>18</sup>	-1.33	NHE	6.50	$DMF + 2 M H_2O$	0.138	$\times 10^3$	2.19	6.29	1.72	-1.89	-	-1.83	0.191
10						3.81							
Fe3 <sup>18</sup>	-1.68	NHE	3.00	$DMF + 2 M H_2O$	0.138	$\times 10^{1}$	2.19	6.29	1.72	-1.89	-	-1.67	0.697
Fe27													
(Fe- <i>o</i> -						1.65							
$F_8)^{13}$	-1.30	NHE	2.20	DMF + 5.5 M H <sub>2</sub> O	0.321	$\times 10^{1}$	1.84	5.31	1.45	-1.89	-	-1.64	0.354
Fe23 <sup>13</sup>	-1.11	NHE	1.25	$DMF + 5.5 M H_2O$	0.321	5.53	1.84	5.31	1.45	-1.89	-	-1.59	0.206

<b>D</b> 40 <sup>12</sup>	1.00		2.00		0.001	1.14	1.0.4			1.00			0.000
Fel313	-1.32	NHE	3.88	$DMF + 5.5 M H_2O$	0.321	$\times 10^2$	1.84	5.31	1.45	-1.89	-	-1.71	0.299
E. 1013	1 1 2	NUE	2.07		0.221	1.13	1.04	5.21	1.45	1.00		1 71	0.102
Fel213	-1.12	NHE	3.87	$DMF + 5.5 M H_2O$	0.321	$\times 10^{2}$	1.84	5.31	1.45	-1.89	-	-1./1	0.102
Eo.415	2 1 2	Eo/Eo	1 25	DMF + 0.1 M	0.001	1.5/	2.50	9 21	2 27		2.15	1.04	0.170
геч	-2.12	ΓC/ΓC+	4.55		0.001	× 10 2.46	2.30	0.31	2.21	-	-2.13	-1.94	0.179
Fe5 <sup>15</sup>	-2.18	Fc/Fc+	6.74	PhOH	0.001	$\times 10^{3}$	2.50	8.31	2.27	_	-2.15	-2.05	0.133
				DMF + 0.1 M		1.37							
Fe6 <sup>15</sup>	-2.15	Fc/Fc+	2.23	PhOH	0.001	$\times 10^{1}$	2.50	8.31	2.27	-	-2.15	-1.85	0.303
				DMF + 0.1 M		8.73							
Fe7 <sup>15</sup>	-2.16	Fc/Fc+	3.84	PhOH	0.001	$\times 10^{1}$	2.50	8.31	2.27	-	-2.15	-1.92	0.242
				DMF + 0.002 M									
Fe1419	-2.10	Fc/Fc+	1.30	PhOH	0.001	4.69	2.50	8.31	2.27	-	-2.15	-2.01	0.095
				DMF + 0.004 M									
Fe14 <sup>19</sup>	-2.10	Fc/Fc+	1.60	PhOH	0.001	6.62	2.50	8.31	2.27	-	-2.15	-1.98	0.117
				DMF + 0.010 M		1.05							
Fe14 <sup>19</sup>	-2.10	Fc/Fc+	2.00	PhOH	0.001	$\times 10^{1}$	2.50	8.31	2.27	-	-2.15	-1.95	0.147
				DMF + 0.020 M		1.62							
Fe14 <sup>19</sup>	-2.10	Fc/Fc+	2.38	PhOH	0.001	$\times 10^{1}$	2.50	8.31	2.27	-	-2.15	-1.94	0.166
10				DMF + 0.040 M		2.35							
Fe14 <sup>19</sup>	-2.10	Fc/Fc+	2.70	PhOH	0.001	$\times 10^{1}$	2.50	8.31	2.27	-	-2.15	-1.91	0.187
10				DMF + 0.002 M									
Fe15 <sup>19</sup>	-2.28	Fc/Fc+	1.25	PhOH	0.001	4.42	2.50	8.31	2.27	-	-2.15	-2.00	0.271
<b>T 1 7</b> 10			1.50	DMF + 0.004 M	0.001		2.50	0.01			2.1.7	1.00	0.001
Fel5 <sup>19</sup>	-2.28	Fc/Fc+	1.52	PhOH	0.001	6.04	2.50	8.31	2.27	-	-2.15	-1.98	0.294
E 1619	2 20		1.65	DMF + 0.010 M	0.001	7.01	2.50	0.21	2.07		2.15	1.04	0.226
Felsi	-2.28	FC/FC+	1.65	PhOH DME + 0.020 M	0.001	/.01	2.50	8.31	2.27	-	-2.15	-1.94	0.336
Fe15 <sup>19</sup>	-2.28	Fc/Fc+	2 20	DMF + 0.020 M PhOH	0.001	$1.32 \times 10^{1}$	2 50	8 31	2 27	_	-2.15	-1 93	0 347
1015	-2.20	10/101	2.20	$DME \pm 0.040 M$	0.001	1.80	2.50	0.51	2.21		-2.15	-1.75	0.547
Fe15 <sup>19</sup>	-2.28	Fc/Fc+	2.47	PhOH	0.001	$\times 10^{1}$	2.50	8 31	2.27	_	-2.15	-1 90	0 371
	2.20			DMF + 0.002 M	0.001			0.01	,			2.20	0.071
Fe16 <sup>19</sup>	-2.09	Fc/Fc+	0.63	PhOH	0.001	2.17	2.50	8.31	2.27	-	-2.15	-1.98	0.111
				DMF + 0.004 M									
Fe16 <sup>19</sup>	-2.09	Fc/Fc+	1.05	PhOH	0.001	3.51	2.50	8.31	2.27	-	-2.15	-1.96	0.128
				DMF + 0.010 M									
Fe16 <sup>19</sup>	-2.09	Fc/Fc+	1.50	PhOH	0.001	5.87	2.50	8.31	2.27	-	-2.15	-1.93	0.155

				DMF + 0.020 M						-			
Fe16 <sup>19</sup>	-2.09	Fc/Fc+	1.88	PhOH	0.001	9.09	2.50	8.31	2.27		-2.15	-1.91	0.174
				DMF + 0.040 M		1.29				-			
Fe16 <sup>19</sup>	-2.09	Fc/Fc+	2.18	PhOH	0.001	$\times 10^{1}$	2.50	8.31	2.27		-2.15	-1.89	0.196
				$DMF + 0.1 M H_2O$		2.26					-		
Fe21 <sup>20</sup>	-1.37	SHE	2.65	+ 0.1 M PhOH	0.008	$\times 10^{1}$	2.48	8.00	2.19	-1.89		-1.66	0.399
				$DMF + 0.1 M H_2O$		9.53					-		
Fe21 <sup>20</sup>	-1.37	SHE	3.90	+ 1.0 M PhOH	0.008	$\times 10^{1}$	2.48	8.00	2.19	-1.89		-1.72	0.344
				$DMF + 0.1 M H_2O$		8.49					-		
Fe21 <sup>20</sup>	-1.37	SHE	3.80	+ 3.0 M PhOH	0.008	$\times 10^{1}$	2.48	8.00	2.19	-1.89		-1.71	0.348
				$DMF + 0.1 M H_2O$							-		
Fe22 <sup>20</sup>	-1.28	SHE	1.38	+ 0.1 M PhOH	0.008	5.21	2.48	8.00	2.19	-1.89		-1.60	0.367
				$DMF + 0.1 M H_2O$		3.38					-		
Fe22 <sup>20</sup>	-1.28	SHE	3.00	+ 1.0 M PhOH	0.008	$\times 10^{1}$	2.48	8.00	2.19	-1.89		-1.68	0.295
				$DMF + 0.1 M H_2O$		5.36					-		
Fe22 <sup>20</sup>	-1.28	SHE	3.40	+ 3.0 M PhOH	0.008	$\times 10^{1}$	2.48	8.00	2.19	-1.89		-1.69	0.277
				$DMF + 0.1 M H_2O$		9.53					-		
Fe23 <sup>20</sup>	-1.12	SHE	-0.10	+ 0.1 M PhOH	0.008	×10 <sup>-1</sup>	2.48	8.00	2.19	-1.89		-1.54	0.274
				$DMF + 0.1 M H_2O$							-		
Fe23 <sup>20</sup>	-1.12	SHE	0.95	+ 1.0 M PhOH	0.008	3.19	2.48	8.00	2.19	-1.89		-1.58	0.228
				$DMF + 0.1 M H_2O$		1.34					-		
Fe23 <sup>20</sup>	-1.12	SHE	2.20	+ 3.0 M PhOH	0.008	$\times 10^{1}$	2.48	8.00	2.19	-1.89		-1.64	0.172
				$DMF + 0.1 M H_2O$		6.75					-		
Fe316	-1.73	SHE	3.60	+ 0.1 M PhOH	0.008	$\times 10^{1}$	2.48	8.00	2.19	-1.89		-1.70	0.717
				$DMF + 0.1 M H_2O$		1.77					-		
Fe18 <sup>20</sup>	-1.26	SHE	4.44	+ 3.0 M PhOH	0.008	$\times 10^2$	2.48	8.00	2.19	-1.89		-1.74	0.218
				$DMF + 0.1 M H_2O$		9.26					-		
Fe19 <sup>20</sup>	-0.94	SHE	5.88	+ 3.0 M PhOH	0.008	$\times 10^2$	2.48	8.00	2.19	-1.89		-1.80	-0.165
				$DMF + 0.1 M H_2O$		7.40					-		
Fe26 <sup>20</sup>	-1.43	SHE	3.68	+ 3.0 M PhOH	0.008	$\times 10^{1}$	2.48	8.00	2.19	-1.89		-1.71	0.417
						1.39					-		
Fe2017	-1.05	NHE	6.05	DMF/H <sub>2</sub> O 9:1	0.323	$\times 10^{3}$	1.83	5.29	1.45	-1.89		-1.81	-0.068
				DMF + 0.1 M		5.51				-			
Fe25 <sup>15</sup>	-2.19	Fc/Fc+	3.44	PhOH	0.001	$\times 10^{1}$	2.50	8.31	2.27		-2.15	-1.90	0.290
				DMF + 0.1 M						-			
Fe2415	-2.00	Fc/Fc+	0.97	PhOH	0.001	3.21	2.50	8.31	2.27		-2.15	-1.79	0.209
				MeCN + 1.0 M		4.37		1.30		-			
Re1 <sup>21</sup>	-1.89	Fc/Fc+	3.60	PhOH	0.001	$\times 10^{1}$	9.05	$ imes 10^2$	5.19		-2.00	-1.67	0.224

				MeCN + 2.8 M				1.32					
Re1 <sup>22</sup>	-2.08	Fc/Fc+	1.41	H <sub>2</sub> O	0.133	3.51	6.71	$\times 10^2$	5.27	-1.75	-	-1.51	0.565
						3.82		1.30					
Re8 <sup>23</sup>	-2.09	Fc/Fc+	3.48	MeCN	0.005	$\times 10^{1}$	8.95	$\times 10^2$	5.21	-1.75	-	-1.60	0.490
Re11													
(Re- <i>p</i> -				MeCN + 1.0 M		5.08		1.30					
OMe) <sup>21</sup>	-1.97	Fc/Fc+	3.73	PhOH	0.001	$\times 10^{1}$	9.05	$\times 10^2$	5.19	-	-2.00	-1.67	0.298
Re12													
(Re- <i>p</i> -				MeCN + 1.0 M		5.47		1.30					
<i>t</i> Bu) <sup>21</sup>	-2.03	Fc/Fc+	3.79	PhOH	0.001	$\times 10^{1}$	9.05	$\times 10^2$	5.19	-	-2.00	-1.67	0.355
Re13													
(Re- <i>p</i> -				MeCN + 1.0 M		5.32		1.30					
Me) <sup>21</sup>	-1.98	Fc/Fc+	3.77	PhOH	0.001	$\times 10^{1}$	9.05	$\times 10^2$	5.19	-	-2.00	-1.67	0.307
						1.13		1.32					
Re9 <sup>22</sup>	-1.90	Fc/Fc+	2.43	MeCN +2.8 M H <sub>2</sub> O	0.133	$ imes 10^1$	6.71	$\times 10^2$	5.27	-1.75	-	-1.56	0.345
								1.32					
Re10 <sup>22</sup>	-1.93	Fc/Fc+	2.14	MeCN +2.8 M H <sub>2</sub> O	0.133	8.12	6.71	$\times 10^2$	5.27	-1.75	-	-1.54	0.388
Mn15													
(Mn-o-				MeCN + 0.5 M		1.20		1.30					
Ph) <sup>24</sup>	-1.92	Fc/Fc+	2.47	PhOH	0.001	$\times 10^{1}$	9.05	$\times 10^2$	5.19	-	-2.00	-1.65	0.268
Mn16													
(Mn-o-				MeCN + 2.0 M		2.07		1.30					
Mes) <sup>24</sup>	-2.29	Fc/Fc+	2.95	PhOH	0.001	$\times 10^{1}$	9.05	$\times 10^2$	5.19	-	-2.00	-1.60	0.688
Mn17													
(Mn-o-													
PhOMe				MeCN + 1.0 M		1.94		1.30					
)24	-1.90	Fc/Fc+	2.89	PhOH	0.001	$\times 10^{1}$	9.05	$\times 10^2$	5.19	-	-2.00	-1.63	0.265
Mn18													
(Mn-o-													
PhOCF				MeCN + 1.3 M				1.30					
3)24	-1.85	Fc/Fc+	1.62	PhOH	0.001	4.50	9.05	$\times 10^2$	5.19	-	-2.00	-1.56	0.285
Mn19													
(Mn-o-													
PhNH <sub>2</sub>				MeCN + 0.7 M		1.97		1.30					
$)^{24}$	-1.96	Fc/Fc+	2.91	PhOH	0.001	$\times 10^{1}$	9.05	$\times 10^2$	5.19	-	-2.00	-1.65	0.306

Mn20 (Mn-o-													
CONH				MeCN + 5.51 M		1.14		1.18					
Me) <sup>25</sup>	-1.91	Fc/Fc+	2.39	$H_2O$	0.242	$\times 10^{1}$	5.25	$ imes 10^2$	4.73	-1.75	-	-1.55	0.356

# S3. Structures of CO<sub>2</sub>-to-CO reduction catalysts assessed in the scaling relationships study

Scheme S1. The molecular catalysts included in our scaling relations analysis. The anionic axial ligand coordinated to the Fe center has been omitted for clarity.













Scheme S1. Continued.





Fe19









Fe21











#### Scheme S1. Continued.



#### S4. Derivation of *m*<sub>[HA]</sub>

The theoretically expected slope ( $m_{[HA]}$ ) of the  $\eta_{eff}$ -log(TOF<sub>max</sub>) plot in Figure 7 can be calculated from the ratio of the first derivatives of the expression for TOF<sub>max</sub> and  $\eta_{eff}$  with respect to [HA] (eq. 15).

$$m_{[HA]} = \frac{\partial \log(TOF_{max})}{\partial \eta_{eff}} = \frac{\partial \log(TOF_{max})/\partial[HA]}{\partial \eta_{eff}/\partial[HA]}$$
(15)

The expression for  $\text{TOF}_{\text{max}}$  is given in eq. 16 where  $k_{\text{cat}}$  is the catalytic rate constant,  $p_{\text{CO2}}$  is the CO<sub>2</sub> partial pressure (equal to 1 atm), and *a* and *b* are the reaction orders of [HA] and  $p_{\text{CO2}}$ , respectively (*a*=*b*=1).

$$TOF_{max} = k_{cat} [HA]^a (p_{CO_2})^b$$
(16)

The conversion of CO<sub>2</sub> to CO in a nonaqueous solvent is given by eq. 17.  $\eta_{eff}$  can be defined based on the Nernst equation.<sup>26</sup> In the CO<sub>2</sub>RR, the equilibrium potential,  $E_{CO2/CO}$  is governed by the Nernst equation given in eq. 18 where n=2.

$$CO_2 + 2H^+ + 2e^- \to CO + H_2O$$
 (17)

$$E_{CO_2/CO} = E^{\circ}_{CO_2/CO} - \frac{2.303RT}{nF} \log\left(\frac{p_{CO}[H_2O]}{p_{CO_2}[H^+]^2}\right)$$
(18)

Since we know the equilibrium constant given by eq. 19, we can expand eq. 18 to include  $log(K_a)$  (eq. 20) which, in turn, leads to the inclusion of the pKa of the acid used (eq. 21)

$$K_a = \frac{[H^+][A^-]}{[HA]} \leftrightarrow [H^+] = \frac{K_a[HA]}{[A^-]}$$
(19)

$$E_{CO_2/CO} = E^{\circ}_{CO_2/CO} - \frac{2.303RT}{2F} \log\left(\frac{p_{CO}[H_2O][A^-]^2}{p_{CO_2}(K_a)^2[HA]^2}\right)$$
(20)

$$E_{CO_2/CO} = E^{\circ}_{CO_2/CO} - \frac{2.303RT}{2F} \log\left(\frac{p_{CO}[H_2O][A^-]^2}{p_{CO_2}[HA]^2}\right) - \frac{2.303RT}{F} pK_a$$
(21)

 $\eta_{\text{eff}}$  can be redefined as in eq. 22, which, when combined with eq. 21, results in the final expression for  $\eta_{\text{eff}}$  as given by eq. 23.

$$\eta_{eff} = E_{CO_2/CO} - E_{cat/2} \tag{22}$$

$$\eta_{eff} = E^{\circ}_{CO_2/CO} - E_{cat/2} - \frac{2.303RT}{2F} \log\left(\frac{p_{CO}[H_2O][A^-]^2}{p_{CO_2}[HA]^2}\right) - \frac{2.303RT}{F} pK_a$$
(23)

The first derivatives of eq. 16 and 23 with respect to [HA] are given by eq. 24 and 25, respectively.

$$\frac{\partial \log(TOF_{max})}{\partial[HA]} = \frac{\partial \log(k_{cat}[HA]^a(p_{CO_2})^b)}{\partial[HA]} = \frac{a}{[HA]\ln(10)}$$
(24)

$$\frac{\partial \eta_{eff}}{\partial [HA]} = \frac{0.0592 \, V}{[HA] \ln \left( 10 \right)} \tag{25}$$

Finally, the ratio of eq. 24 and 25 results in a theoretical slope of 16.9 dec/V (eq. 26).

$$m_{[HA]} = \frac{\partial \log(TOF_{max})/\partial[HA]}{\partial \eta_{eff}/\partial[HA]} = \frac{a}{0.0592} dec/V = 16.9 dec/V$$
(26)

#### S5. Additional figures



 $\label{eq:Figure S2.} \mbox{ log(TOF}_{max}) \mbox{ as a function of } \eta_{eff} \mbox{ for all the catalysts analyzed in this study. The best-performing catalysts are highlighted in purple.}$ 



**Figure S3.** Linear scaling relation for Re bipyridine catalysts **Re1**, **Re11** (–OMe), **Re13** (–Me), and **Re12** (–*t*Bu) showing the effect of changing  $E_{cat/2}$ . The catalysts were tested in the presence of 1.0 M phenol. The slope obtains a value of 1.54 dec V<sup>-1</sup>.



Figure S4.  $log(TOF_{max})$  as a function of  $\eta_{eff}$  showing the best-performing catalysts in this study (Fe2, Fe5, Fe12, Fe19, and Fe20) and the scaling relation is set by Fe24, Fe1, and Fe25.

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