Electronic Supplementary Information

Electrocatalytic proton-reduction behaviour of telluride-capped triiron clusters: tuning of overpotentials and stabilization of redox states relative to lighter chalcogenide analogues

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Figure S1. (a) CVs of $[Fe_3(CO)_7(\mu_3-Te)_2(\mu-dppa)]$ (6) at various scan rates in CH₂Cl₂ (b) CVs of $[Fe_3(CO)_7(\mu_3-Te)_2(\mu-dppa)]$ (6) in the presence of tosylic acid (TsOH) in CH₂Cl₂.

Figure S2. CVs of $[Fe_3(CO)_7(\mu_3-Te)_2(\mu-dppm)]$ (4) in MeCN.

Figure S3. Cyclic voltammograms of 1, 3, 4, 5, 6 in CH₂Cl₂ in the absence and presence of TsOH.

Figure S4. Cyclic voltammograms of $[Fe_3(CO)_9(\mu_3-Te)_2]$ (**1**) in CH_2Cl_2 in the absence and presence of trifluoroacetic acid (TFA).

Figure S5. Cyclic voltammograms of **1** in CH_2Cl_2 with the addition of 0.2-5.0 equivalents of TFA.

Figure S6. Cyclic voltammograms of **1** in CH_2Cl_2 with the addition of up to 14 equivalents of TFA.

Figure S7. Cyclic voltammograms of $\mathbf{1}$ in CH_2Cl_2 with the addition of up to 150 equivalents of TFA.

Figure S8. Spectroelectrochemical IR measurement of the reduction of $[Fe_3(CO)_9(\mu_3-Te)_2]$ (1).

Figure S9. Thin-layer cyclic voltammogram (TL-CV) trace recorded during IR monitoring of the controlled potential electrolysis of $[Fe_3Te_2(CO)_9]$ (**1**).

Figure S10. Experimental and calculated mass spectra of $[Fe_3(CO)_7(\mu_3-Te)_2(\mu-dcpm)]$ (5).

Figure S11. Experimental and calculated mass spectra of $[Fe_3(CO)_7(\mu_3-Te)_2(\mu-dppa)]$ (6).

Table S1: Selected atomic charges and Wiberg bond indices for $[Fe_3(CO)_9(\mu_3-Te)_2]$ (1).

Table S2: Selected atomic charges and Wiberg bond indices for $[Fe_3(CO)_9(\mu_3-Te)_2]$ (1).

Table S3: Computed and experimental bond distances for $[Fe_3(CO)_9(\mu_3-Te)_2]$ (1).

Derivation of electrocatalytic rate constants for proton reduction.



Figure S1a. Cyclic voltammograms of $[Fe_3(CO)_7(\mu_3-Te)_2(\mu-dppa)]$ (6) in CH₂Cl₂ (1 mM solution at 10, 25, 50, 100, 250, 500, 1000, and 2000 mV s⁻¹). Both reductions and the oxidation are chemically irreversible.



Figure S1b. Cyclic voltammograms of $[Fe_3(CO)_7(\mu_3-Te)_2(\mu-dppa)]$ (6) upon addition of 1–32 molar equivalents of TsOH (1 mM solution in CH₂Cl₂, supporting electrolyte [NBu₄][PF₆], scan rate 0.20 Vs⁻¹, 2 mm glassy carbon electrode, potential vs. Fc⁺/Fc); the inset shows a plot of peak current near -1.14, -1.61 volts as TsOH is added. Dilution corrections have been made so that the figures represent the results at constant volume.



Figure S2. Cyclic voltammograms of $[Fe_3(CO)_7(\mu_3-Te)_2(\mu-dppm)]$ (4) in MeCN (1 mM solution at 10, 25, 50, and 250 mV s⁻¹). Reversible reductions occur at -1.28 and -1.70 volts. The oxidation is irreversible.



(a)



(b)



(c)



(d)



(e)

Figure S3. Cyclic voltammograms of **1**, **3**, **4**, **5**, **6** in CH_2Cl_2 in the absence (blue) and presence (red) of TsOH. Also shown is a scan (green) of the same concentration of acid without the complex, indicating that the catalysts make the reduction potential less negative and increase the turnover rate.

- (a) 38 equivalents of TsOH with 1
- (b) 26 equivalents of TsOH with 3
- (c) 38 equivalents of TsOH with 4
- (d) 38 equivalents of TsOH with 5
- (e) 32 equivalents of TsOH with 6

Other conditions are 0.25 V/s scan rate, 0.1M supporting electrolyte [NBu₄][PF₆], a 2 mm glassy carbon electrode, and approximately 1 mM complex.



Figure S4. Cyclic voltammograms of **1** in CH_2Cl_2 in the absence (blue) and presence (red) of 20 equivalents of trifluoroacetic acid (TFA.) Also shown is a scan (green) of the same concentration of acid without the complex, indicating that the catalyst makes the reduction potential less negative. Other conditions are 0.20 V/s scan rate, 0.1M supporting electrolyte [NBu₄][PF₆], a 2 mm glassy carbon electrode, and approximately 1 mM complex.



Figure S5. Cyclic voltammograms of **1** in CH_2Cl_2 with the addition of 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.8 and 5.0 equivalents of TFA. As acid is initially added the second reduction peak shifts to a less negative potential. Other conditions are 0.20 V/s scan rate, 0.1M supporting electrolyte $[NBu_4][PF_6]$, a glassy carbon electrode, and 1 mM complex.



Figure S6. Cyclic voltammograms of **1** in CH_2Cl_2 with further addition of TFA. The first reduction peak increases but the new (See Fig S5) second reduction peak increases much more. Other conditions are 0.20 V/s scan rate, 0.1M supporting electrolyte [NBu₄][PF₆], a glassy carbon electrode, and 1 mM complex.



Figure S7. Cyclic voltammograms of **1** in CH_2Cl_2 with large additions of TFA. The first reduction peak increases but the new (See Fig S5) second reduction peak increases much more while it shifts more negative. The peak beyond 2.0 volts matches the uncatalyzed proton reduction as seen in Fig. S4. Other conditions are 0.20 V/s scan rate, 0.1M supporting electrolyte [NBu₄][PF₆], a glassy carbon electrode, and 1 mM complex.

Spectroelectrochemical IR measurements of the reduction of [Fe₃Te₂(CO)₉]

 $[Fe_3Te_2(CO)_9]$ (1) was founds to be reduced to the stable (ca. 30 minutes under inert IR SEC conditions) anion 1⁻. Further reduction generated 1²⁻ which rapidly pacified the electrode, preventing further monitoring.



Figure S8. IR spectroelectrochemical monitoring of the reduction of **1** to generate **1**⁻ and **1**²⁻. Conditions: 2mM solution, DCM/TBAF, room temperature OTTLE cell



Figure S9. Thin-layer cyclic voltammogram (TL-CV) trace recorded during IR monitoring of the controlled potential electrolysis of $[Fe_3Te_2(CO)_9]$ (1). Arrows mark potentials at which the potential was held constant in order to monitor formation of the respective reduced species

Experimental details:

The spectroelectrochemical measurements were conducted with an optically transparent thin-layer electrochemical (OTTLE) cell (Spectroelectrochemistry Reading) at room-temperature. OTTLE cell was equipped with a Pt minigrid working electrode, a Pt minigrid counter electrode, an Ag wire pseudoreference electrode and CaF2 windows. Infrared spectroelectrochemical experiments were performed on a Bruker Vertex 70v FTIR spectrometer, equipped with either a DTLaGS detector. The electrochemical response in the form of a thin-layer cyclic voltammogram (TL-CV) at v = 5 mV s⁻¹ was recorded with an EmStat3 potentiostat (PalmSens) during IR monitoring of the controlled potential electrolysis.



Figure S10. (a) Experimental mass spectrum of $[Fe_3(CO)_7(\mu_3-Te)_2(\mu-dcpm)]$ (5).



Figure S10. (b) Experimental and calculated high resolution mass spectra of $[Fe_3(CO)_7(\mu_3-Te)_2(\mu-dcpm)]$ (5).



Figure S11. Experimental and calculated high resolution mass spectra of $[Fe_3(CO)_7(\mu_3-Te)_2(\mu-dppa)]$ (6).

charge	Fe ₁	Fe ₂	Fe ₃	Te ₄	Te ₅
227451	-1.80	-1.80	-1.78	0.74	0.74
227628	-1.80	-1.54	-1.77	0.51	0.51
227545	-1.78	-1.77	-1.64	-0.05	0.55
227589	-1.61	-1.73	-1.68	-0.34	0.36

Table S1: Selected atomic charges and Wiberg bond indices for the computed structure of $[Fe_3Te_2(CO)_9]$

Table S2: Selected atomic charges and Wiberg bond indices for the computed structure of $[Fe_3Te_2(CO)_9]$

WBI	Fe ₁ -Fe ₂	Fe ₁ -Fe ₃	Fe ₂ -Fe ₃	Fe ₁ -Te ₄	Fe ₂ -Te ₄	Fe ₃ -Te ₄	Fe ₁ -Te ₅	Fe ₂ -Te ₅	Fe ₂ -Te ₅
227451	0.04	0.35	0.35	0.88	0.88	0.68	0.87	0.87	0.75
227628	0.02	0.37	0.04	0.78	0.79	0.76	0.78	0.79	0.76
227545	0.04	0.37	0.37	0.74	0.74	0.05	0.76	0.76	0.88
227589	0.02	0.08	0.16	0.77	0.73	0.64	0.77	0.71	0.71

Bond	Observed (X-Ray, Å)	Calculated (Å)
Te(1)-Fe(1)	2.527(2)	2.58266
Te(1)-Fe(2)	2.524(2)	2.58293
Te(1)-Fe(3)	2.550(2)	2.61329
Te(2)-Fe(1)	2.528(2)	2.58979
Te(2)-Fe(2)	2.532(2)	2.58932
Te(2)-Fe(3)	2.531(2)	2.63213
Fe(1)-C(1)	1.81(1)	1.81262
Fe(1)-C(2)	1.82(2)	1.81172
Fe(1)-C(3)	1.80(1)	1.78005
Fe(2)-C(4)	1.80(1)	1.81258
Fe(2)-C(5)	1.82(1)	1.81175
Fe(2)-C(6)	1.78(1)	1.77998
Fe(3)-C(7)	1.76(1)	1.77889
Fe(3)-C(8)	1.80(2)	1.77884
Fe(3)-C(9)	1.78(1)	1.78994
C(1)-O(1)	1.13(2)	1.14534
C(2)-O(2)	1.13(2)	1.14504
C(3)-O(3)	1.14(2)	1.14721
C(4)-O(4)	1.14(2)	1.14536
C(5)-O(5)	1.13(2)	1.14494
C(6)-O(6)	1.15(2)	1.14725
C(7)-O(7)	1.18(2)	1.14804
C(8)-O(8)	1.16(2)	1.15171
C(9)-O(9)	1.15(2)	1.15172

 Table S3: A comparison of computed and observed bond distances for [Fe₃Te₂(CO)₉] (1).

Derivation of electrocatalytic rate constants for proton reduction

It is expected (J. Am. Chem. Soc. 2006, 128, 358-366) for a catalytic reaction that is second order in acid and first order in catalyst concentration that $\frac{i_c}{i_p} = \frac{n}{0.4463} \sqrt{\frac{RTk}{F_{\upsilon}}} \left[H^+ \right]$ for rapid

electron transfer and acid concentrations sufficiently high that they are unchanged during the course of the reaction. Thus, plotting i_c/i_p as a function of [H⁺] should be linear with

$$s/ope = \frac{n}{0.4463} \sqrt{\frac{RTk}{Fv}}$$
 which rearranges to give $k = \frac{Fv}{RT} \left(\frac{s/ope \times 0.4463}{n}\right)^2$, where i_c is the

catalytic current, i_p is the peak current measured for the catalyst in the absence of acid, n=2 is the number of electrons involved in the catalytic reaction with rate constant k for hydrogen production, R is the universal gas constant, T is the temperature in Kelvin, F is Faraday's constant, v is the scan rate and .4463 is a constant determined by numerical solution of the diffusion equations.

As an example, the calculation for the second wave of complex 5 yields

$$k = \frac{\left(\frac{96485 \times \text{coulomb}}{\text{mol}}\right) \left(\frac{0.250 \times \text{volt}}{\text{sec}}\right)}{\left(\frac{8.3145 \times \text{volt} \times \text{coulomb}}{\text{K} \times \text{mol}}\right) (293 \times \text{K})} \left(\frac{\frac{0.6549}{10^{-3} \text{M}} \times 0.4463}{2}\right)^2 = \frac{2.1 \times 10^5}{\text{M}^2 \text{sec}}$$