

Supplementary Information:

Controlling product selectivity in oxidative desulfurization using an electrodeposited iron film.

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All computational structures can be found at <https://github.com/fredingroup/DBToxidation.git>

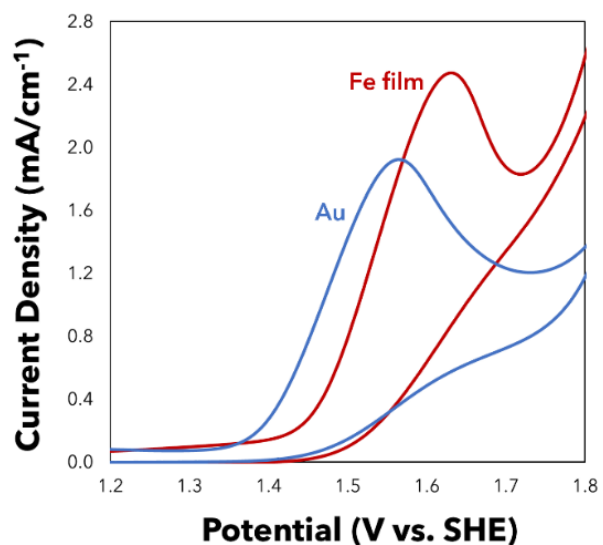


Figure S1. Comparison of cyclic voltammograms for DBT oxidation using a Au electrode and electrodeposited Fe film. 10 mM DBT in 0.1 M NH₄PF₆ in ACN. Pseudo-Ag/Ag⁺ reference electrode, coiled Pt wire counter, 20 mV/s scan rate.

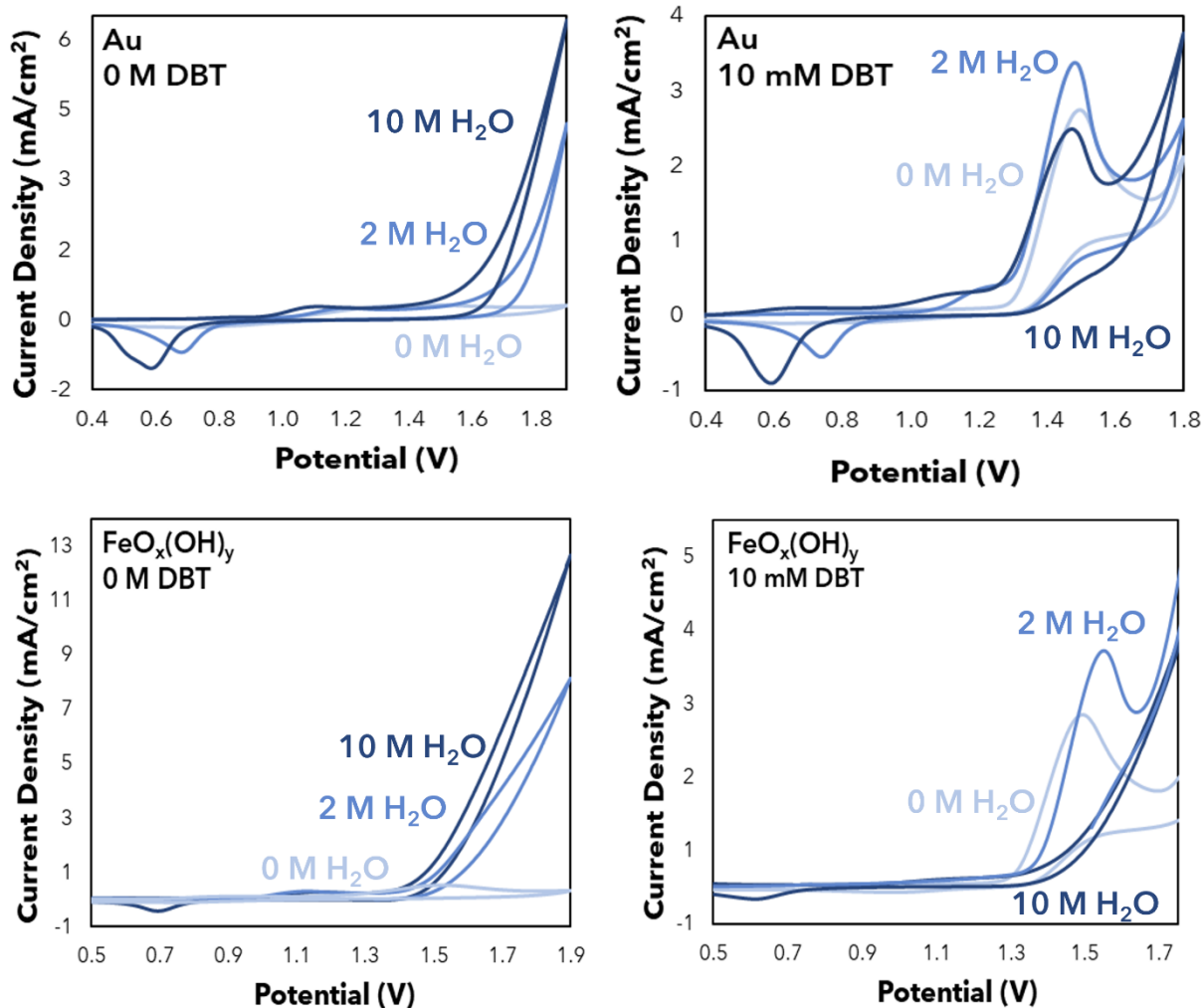


Figure S2. Cyclic voltammograms in 0, 2, and 10 M water electrolytic conditions in the absence and presence (10 mM) of DBT for Au (top) and FeO_x(OH)_y film (bottom). 0.1 M NH₄PF₆ in ACN electrolyte, pseudo-Ag/Ag⁺ reference electrode, coiled Pt wire counter, 20 mV/s scan rate.

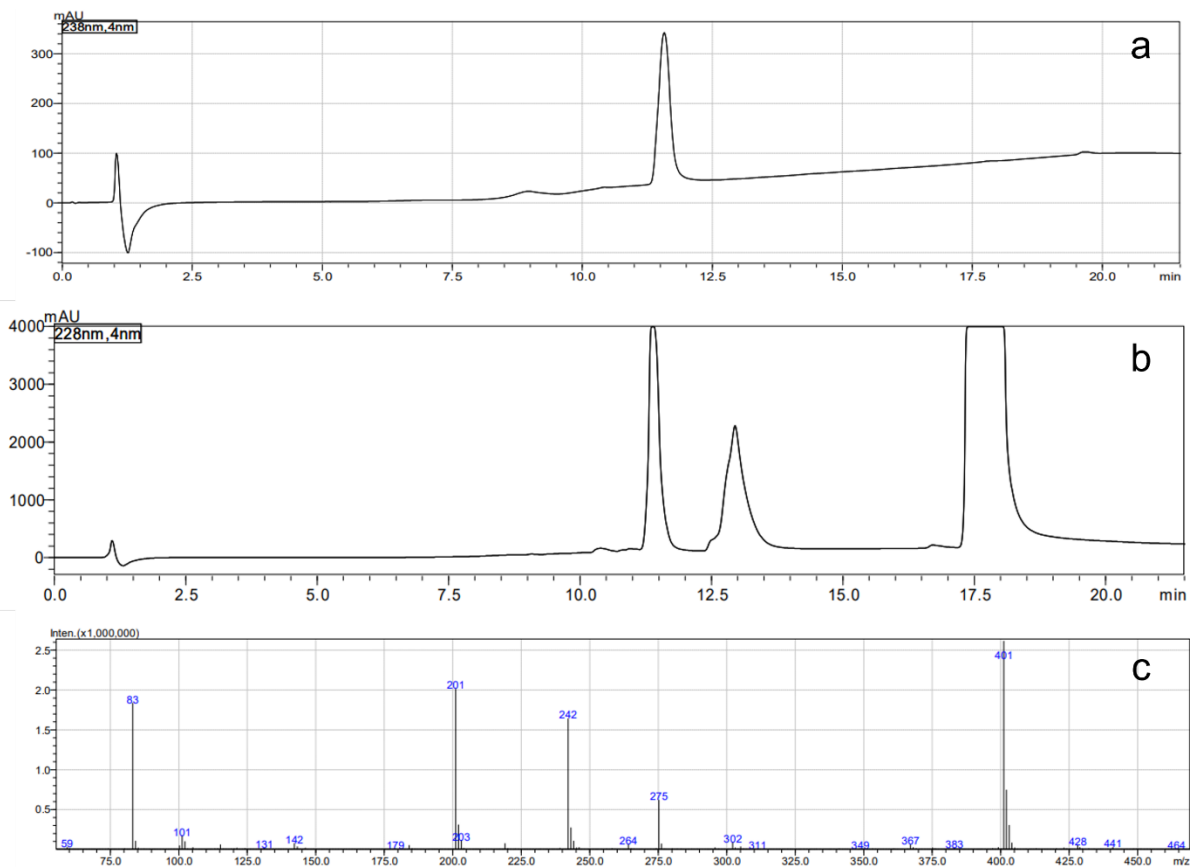


Figure S3. (a) Liquid chromatogram of standard DBTO compared to (b) a typical spectrum post-electrolysis, showing the presence of DBTO in the product, alongside DBT dimer (ret time ~13.0 min) and remaining DBT (ret time ~18.0 min). (c) Mass spectrum obtained at a retention time of 11.5 min from spectrum (b), showing a m/z peak at 201, which corresponds to DBTO. Reverse phase LCMS obtained using a water-acetonitrile gradient.

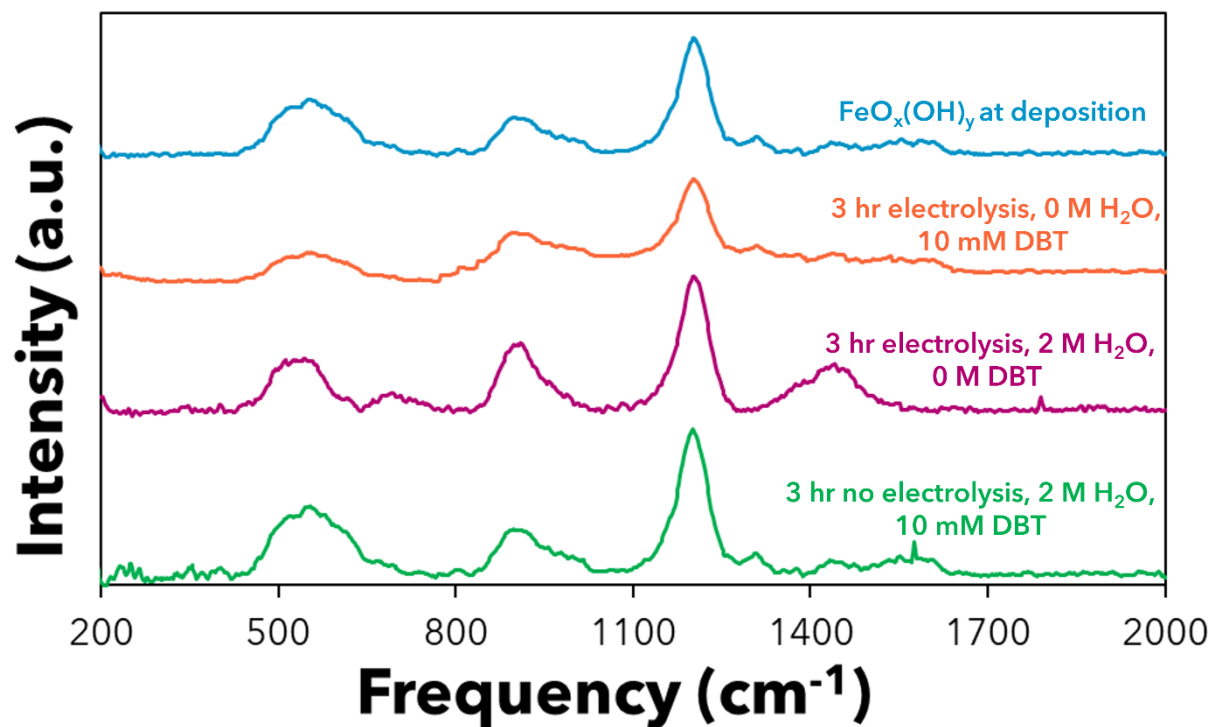


Figure S4. Raman spectra of the FeO_x(OH)_y film upon deposition and after three hours under different experimental conditions. Power: 221 mW, wavelength: 785 nm.

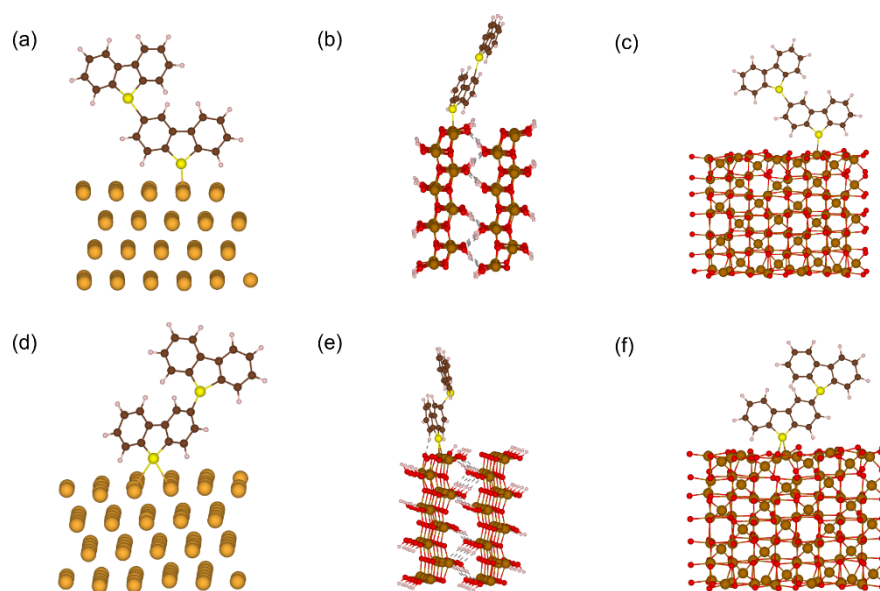


Figure S5. DBT-dimer optimized unit cells for monodentate and bidentate gold (111) (a & d), maghemite (001) (b&e), and lepidocrocite (010) (c&f).

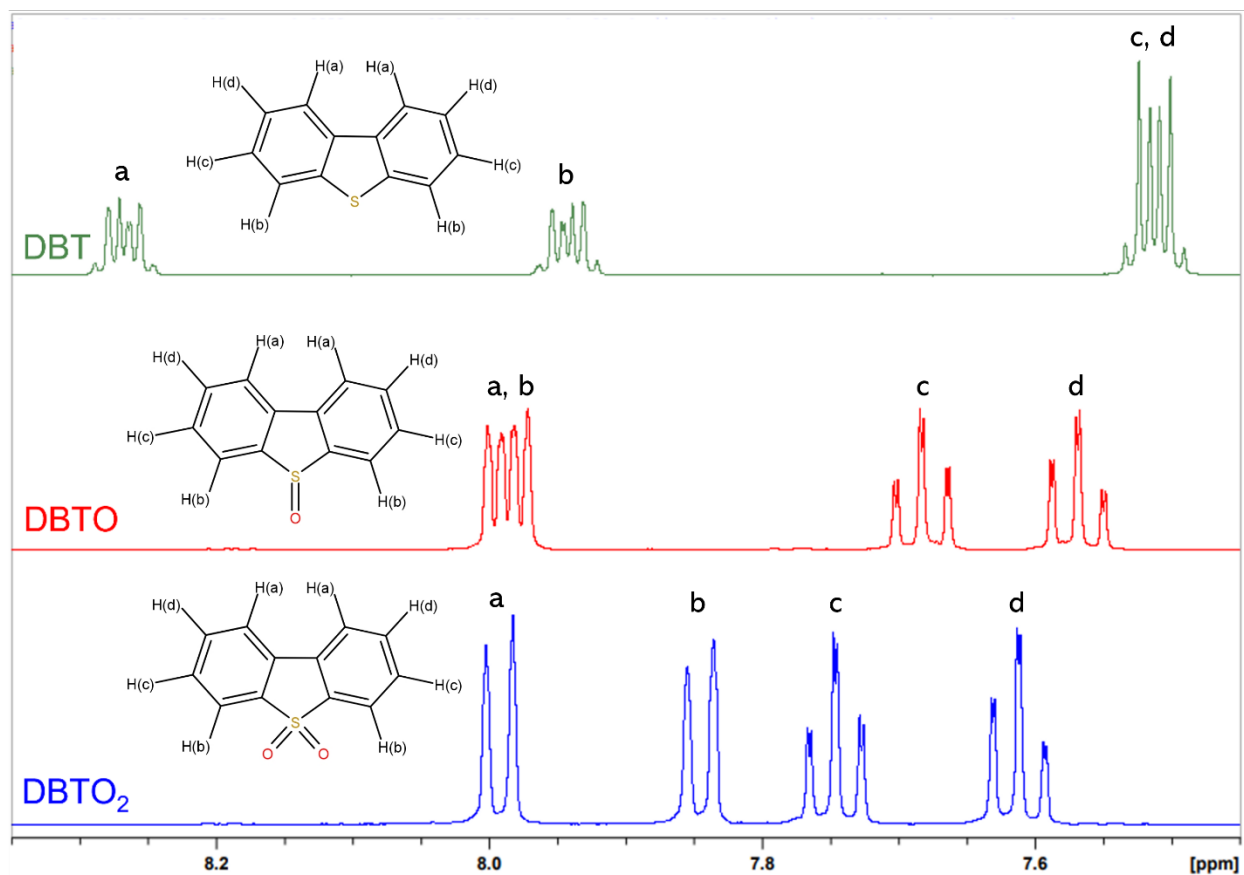


Figure S6. Standard NMR spectra for DBT and common oxidation products DBTO and DBTO₂. Obtained using a 400 MHz NMR in CD₃CN.

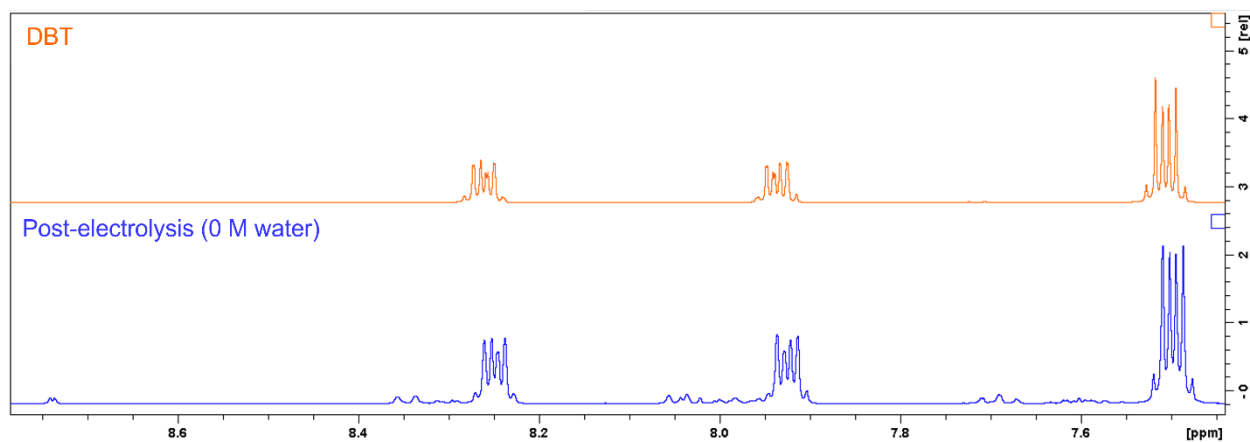


Figure S7. NMR spectrum displaying peak positions for DBT dimer (7.60, 7.69, 8.04, 8.35 and 8.74), the sole oxidation product in the absence of water. Obtained using a 400 MHz NMR in CD_3CN .

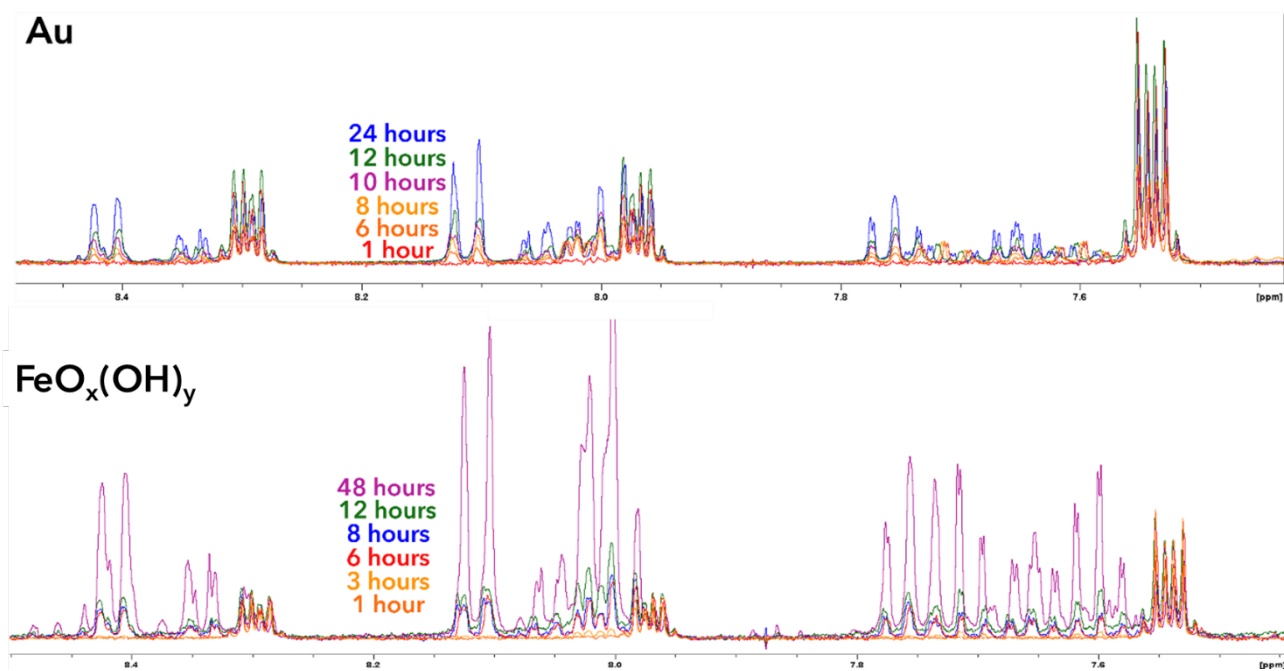


Figure S8. NMR spectra at various time points throughout electrolysis of DBT using Au (top) and $\text{FeO}_x(\text{OH})_y$ film (bottom). Au yields more prominent dimer peaks, while the Fe film shows a mixture of dimer and DBTO.

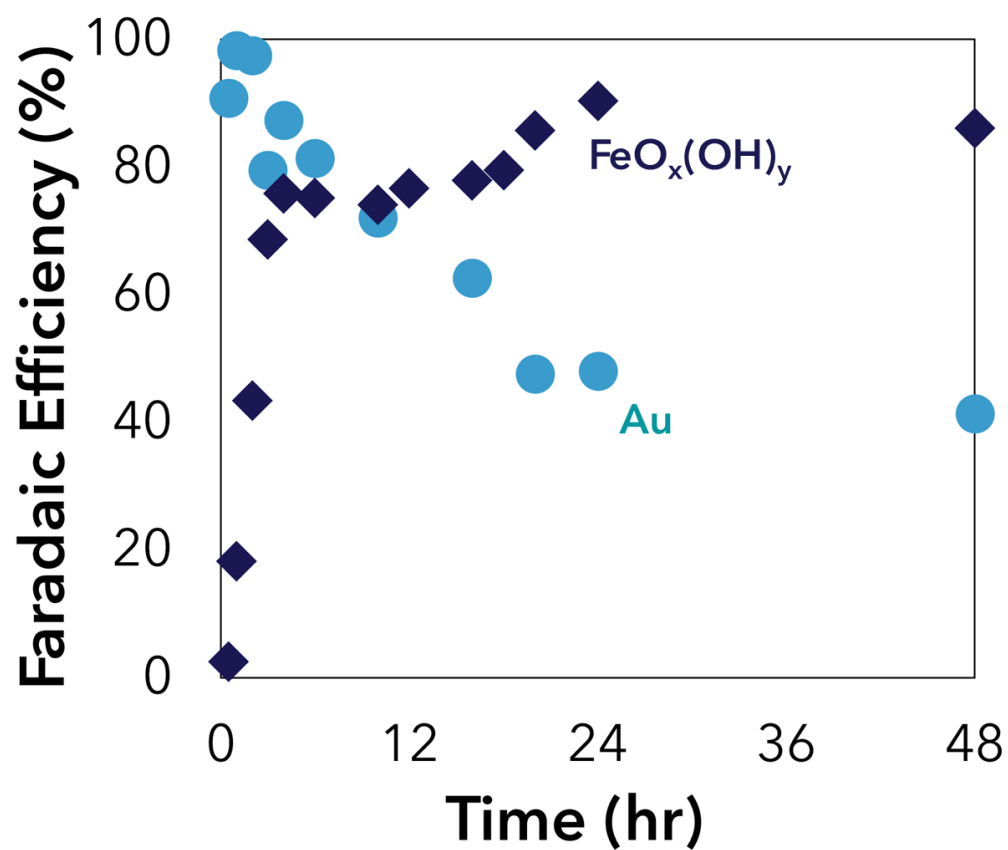


Figure S9. Faradaic efficiencies for DBTO and DBT dimer production at all times aliquots were collected, showing the degradation of Au's efficiency over time and the induction period for the Fe film.

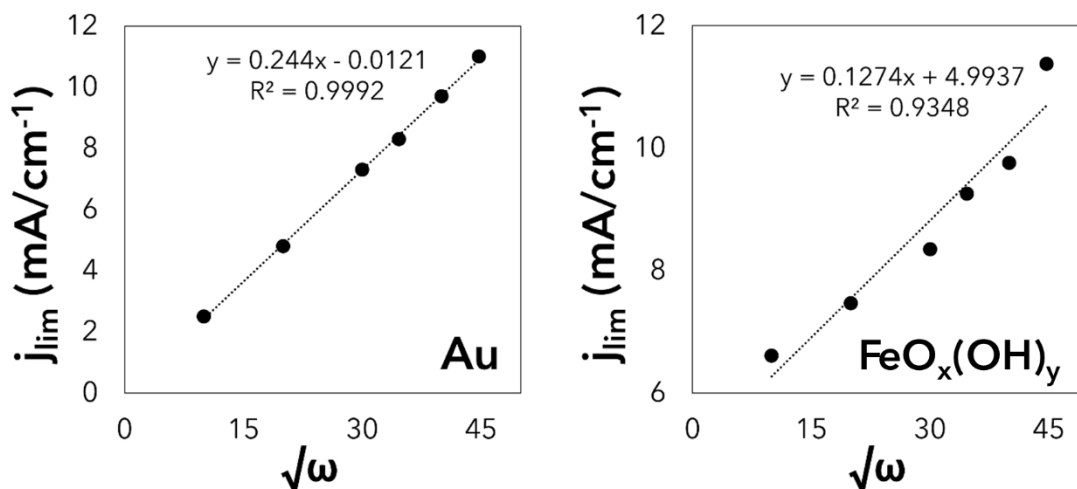


Figure S10. Limiting current density obtained from Linear Sweep Voltammograms at different rotational speeds for the Au and FeO_x(OH)_y film working electrodes.

Table S1. Resulting values from the limiting current density at different rotational rates, demonstrating the higher apparent concentration of DBT at the gold electrode compared to the Fe film.¹

Working Electrode	Slope of limiting current density vs rotation rate plot	Apparent concentration of DBT (mM)
Au	0.244	2.10
Fe film	0.127	0.75

Table S2. PBEsol energies (in eV) and Fe-S Bond lengths (in Å) for the different surfaces and adsorbates

	Surface	clean surface	DBT monomer	DBT-dimer	DBT+ surface	DBT-dimer +surface	DBT monomer +surface -1e ⁻ (oxidized)	Fe-S (DBT+surface)	Fe-S (DBT-dimer +surface)	Fe-S (DBT monomer +surface -1e ⁻ (oxidized))
Monodentate	Y-FeOOH (010)	-1724.53	-145.56	-284.19	-1875.75	-2009.54	-1876.85	2.23	2.42	2.23
	Y-Fe ₂ O ₃ (001)	-1570.76	-145.56	-284.78	-1718.06	-1858.02	-1719.60	2.48	2.54	2.46
	Gold (100)	-370.00	-145.56	-284.68	-515.88	-655.10	-514.95	2.41	2.40	2.40
Bidentate	Y-FeOOH (010)	-1724.53	-145.56	-284.90	-1869.26	-1999.48	-1869.95	2.57, 2.83	2.47, 2.62	2.57, 2.83
	Y-Fe ₂ O ₃ (001)	-1570.76	-145.56	-284.90	-1716.24	-1854.57	-1716.56	2.48, 2.50	2.52, 2.73	2.51, 2.45
	Gold (100)	-370.00	-145.56	-284.90	-515.96	-655.17	-516.01	2.86, 2.84	2.70, 2.82	2.63, 2.82

Table S3. PBEsol energies for DBT-dimer adsorption in different configurations

Surfaces	Monodentate (kJ/mol)	Bidentate (kJ/mol)
γ -FeOOH (010)	-79.72	960.51
γ -Fe ₂ O ₃ (001)	-246.08	105.01
Au (111)	-39.70	-25.47

Table S4. Calculated Bader charges of DBT/DBT-dimer adsorbed on each surface, relative to the isolated molecule.

Surfaces	Monodentate		Bidentate	
	Q _{DBT}	Q _{DBT-dimer}	Q _{DBT}	Q _{DBT-dimer}
Y-FeOOH (010)	+7.6	+14.1	+7.6	+14.2
Y-Fe ₂ O ₃ (001)	+4.8	+11.5	+7.5	+11.6
Au (111)	+7.8	+12.6	+7.8	+14.6

References

1. C. Hamman, A. Hamnett, W. Vielstich. *Electrochemistry*, Electrical Potentials and Electrical Current, pp. 193-194, Wiley-VCH, 2007.