

Electrochemical hydrogen production in aqueous micellar solution by a diiron benzenedithiolate complex relevant to [FeFe] hydrogenases

François Quentel, Guillaume Passard and Frederic Gloaguen*

Electronic Supplementary Information

Fig. S1. Plots of absorbance at λ_{max} versus concentration of $\text{Fe}_2(\text{bdt})(\text{CO})_6$ (**1**) in aqueous solution.

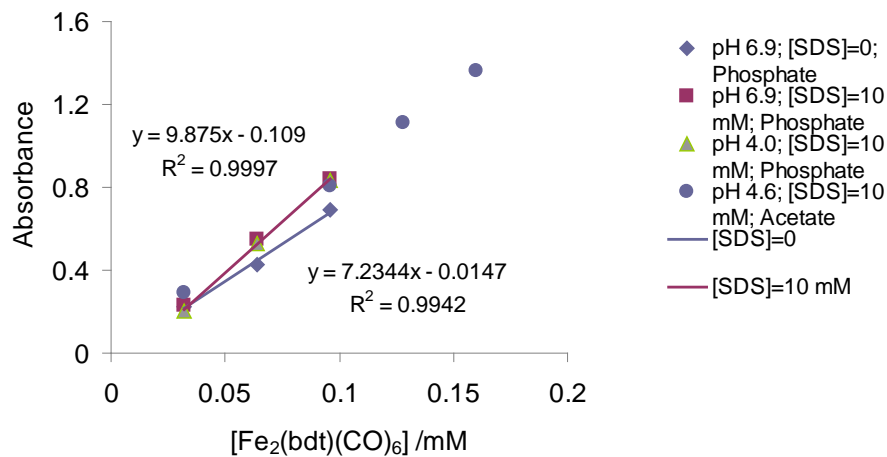


Table S1. Influence of SDS concentration, pH, and the buffer constituents on the absorbance of aqueous solution of **1**.

Buffer	pH	[SDS] /mM	$\lambda_{\text{max}} / \text{nm}$	$\epsilon / \text{M}^{-1} \text{cm}^{-1}$
Phosphate	6.9	0.0	346.5	7234
Phosphate	6.9	1.7	337.5	
Phosphate	6.9	10	335.0	9531
Phosphate	6.9	50	335.5	7289
Phosphate	4.0	10	335.0	9875
Acetate	4.7	10	335.0	10047

Fig. S2. Differential pulse voltammetry (1st scan) of **1** at a freshly polished glassy carbon electrode in 0.1 M phosphate solution. pH was decreased by addition of strong acid. The peak current is poorly responsive to [**1**] indicating strong adsorption of the catalyst on the electrode surface, especially in the presence of SDS (see also Table S2 below). Measurements were carried out at with a scan rate of 2.5 mV s⁻¹ and amplitude of 50 mV. The electrode was 0.071 cm² in surface area.

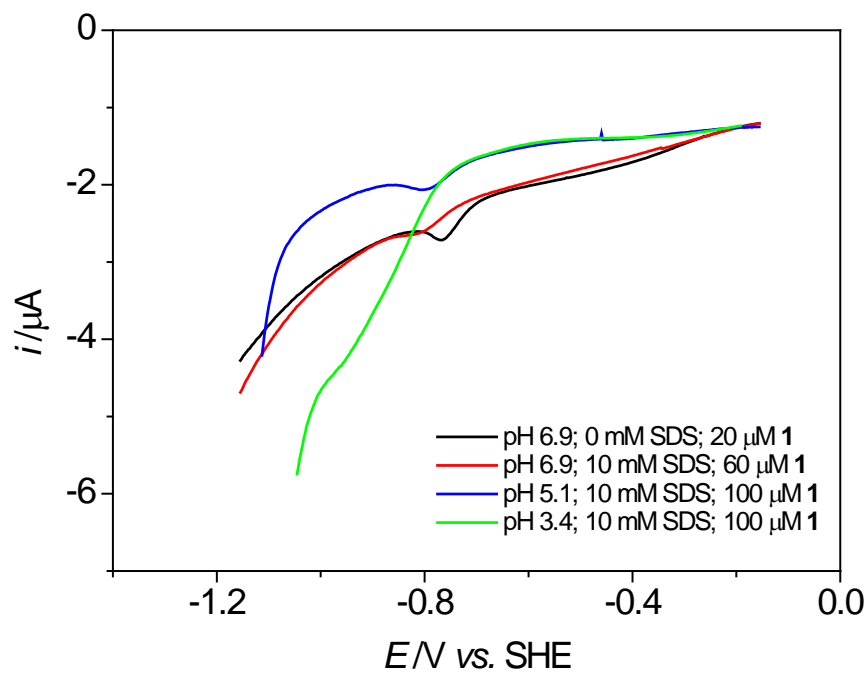


Table S2. Effect of the concentration of **1** and SDS in 0.1 M phosphate buffer on the peak current and potential recorded at a glassy carbon electrode (see Figure S2).

[1] /μM	[SDS] /mM	- <i>i</i> _p /μA	- <i>E</i> _p /V vs. SHE	pH
20	0	0.19	0.69	6.9
20	1.25	0.23	0.77	6.9
40	1.25	0.31	0.77	6.9
60	1.25	0.31	0.77	6.9
60	10	0.12	0.80	6.9
100	10	0.23	0.80	6.9
100	10	0.22	0.79	6.0
100	10	0.21	0.79	5.1

Fig. S3. Differential pulse polarography of $\text{Fe}(\text{SO}_4)_4$ in 0.1 M phosphate buffer solution containing 10 mM SDS. Measurements were carried out at a dropping mercury electrode 0.0052 cm^2 in surface area with a scan rate of 2.5 mV s^{-1} and amplitude of 50 mV. pH was decreased by addition of strong acid. Stars indicate voltammetric peaks due to the presence of SDS.

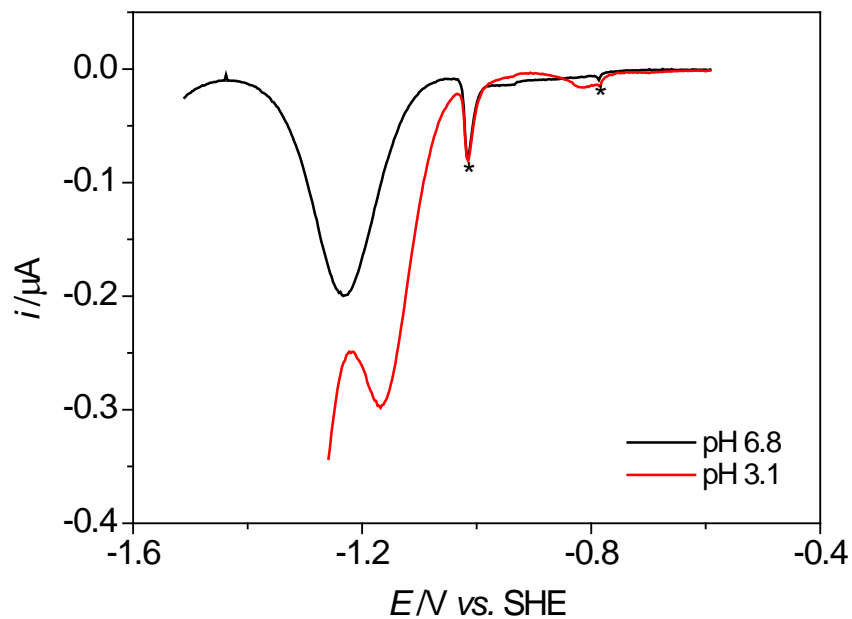


Fig. S4. Plot of the current enhancement versus the scan rate measured for 20 μM **1** in 0.1 M NaCl containing 10 mM SDS and 10 mM acetic acid. Experiments were carried out at a hanging mercury electrode of 0.0052 cm^2 in surface area.

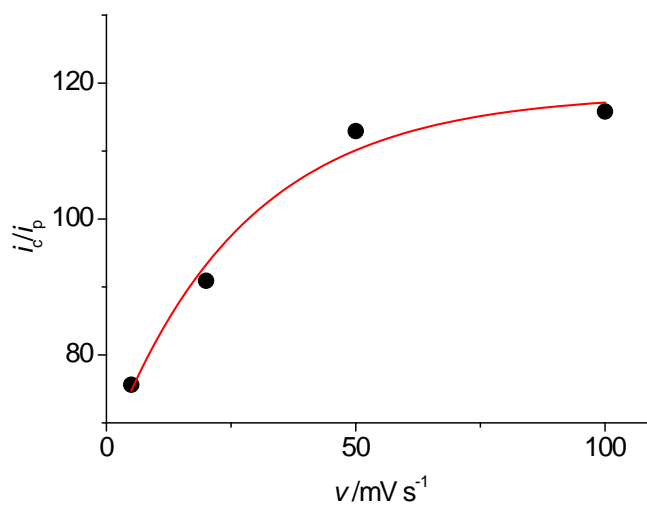


Fig. S5. Charge built-up versus time for electrolysis at -0.66 V vs. SHE of $8\text{ }\mu\text{M}$ **1** in 0.1 M NaCl containing 10 mM SDS and 50 mM acetic acid (pH 3.0). The blue and green traces correspond to the charge built-up in absence of **1** at a fresh and used Hg pool electrode, respectively. Detection of a low activity at the used electrode indicates slight adsorption of **1** during electrolysis.

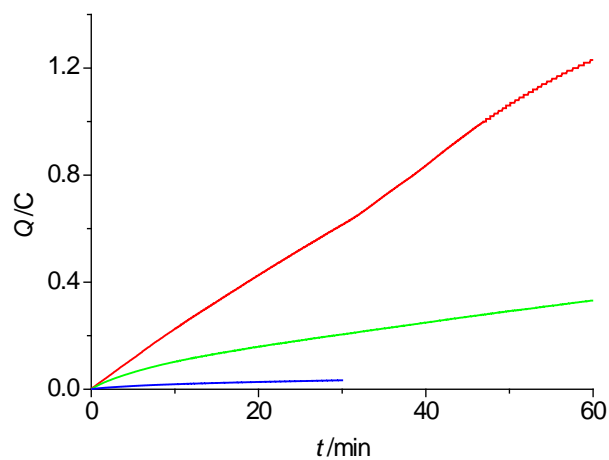


Fig. S6. Charge built-up versus time for electrolysis at -0.66 V vs. SHE of $80\text{ }\mu\text{M}$ **1** in 0.1 M NaCl containing 10 mM SDS and 1 mM HCl. The blue trace corresponds to the charge built-up in absence of **1**. The total charge passed during electrolysis of 10 mL of solution after correction of the blank is $Q_{\text{tot}} = 0.513$ C. This corresponds to the consumption of $Q_{\text{tot}}/F \times 100 = 5.32 \times 10^{-4}$ M of H^+ . In the meantime, pH has increased from 3.23 to 4.30 corresponding to a decrease of $10^{-3.23} - 10^{-4.30} = 5.39 \times 10^{-4}$ M of H^+ . Comparison of these results allows us to conclude that catalyst **1** works at close to 100% Faradaic efficiency.

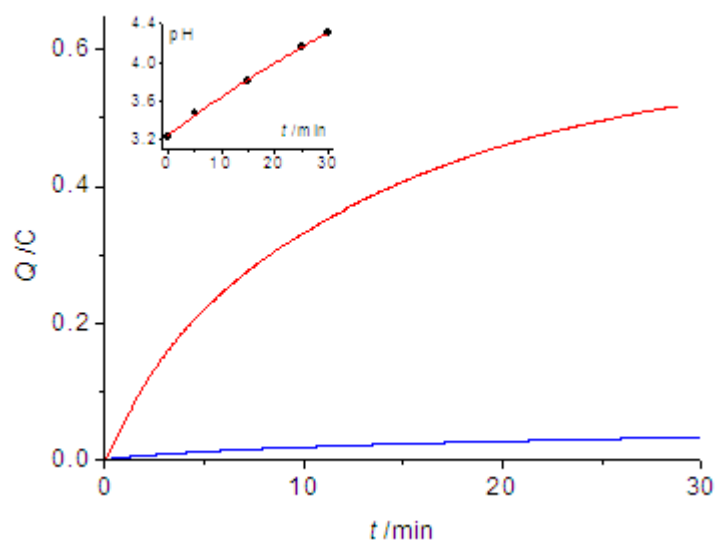


Table S3. Catalytic activity of **1** for H₂ production in aqueous SDS and acetonitrile solutions using acetic acid (HOAc) or toluenesulfonic acid (HOTs) as proton source: activation overpotential (η), current enhancement (i_c/i_p), and mole of H₂ per mole of catalyst (TON).

Acid (pK _a) / Solvent	- η/V	i_c/i_p	TON (duration)	Ref
HOAc (4.8)/ H ₂ O	0.45 ^a	80	52 (1 hour)	this work
HOTs (8.7) / CH ₃ CN	0.60 ^b	< 3	2.8 (2 hours)	S1
HOAc (22.3) / CH ₃ CN	0.64 ^b	14	5.5 (1/2 hour) ^c	S2

^(a) $\eta = E_{1/2} + 0.059 \times \text{pH}$. ^(b) Calculated according the method described in Ref S3. ^(c) Most of the catalyst was decomposed after a period of half an hour.

References

- S1. J. F. Capon, F. Gloaguen, P. Schollhammer and J. Talarmin, *J. Electroanal. Chem.*, 2006, **595**, 47.
- S2. G. A. N. Felton, A. K. Vannucci, J. Chen, L. T. Lockett, N. Okumura, B. J. Petro, U. I. Zakai, D. H. Evans, R. S. Glass and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 2007, **129**, 12521.
- S3. G. A. N. Felton, R. S. Glass, D. L. Lichtenberger and D. H. Evans, *Inorg. Chem.*, 2006, **45**, 9181.