

Supplementary information for

**Electrocatalytic hydrogen production with [FeFe]-Hydrogenase mimics by tetracene derivatives**

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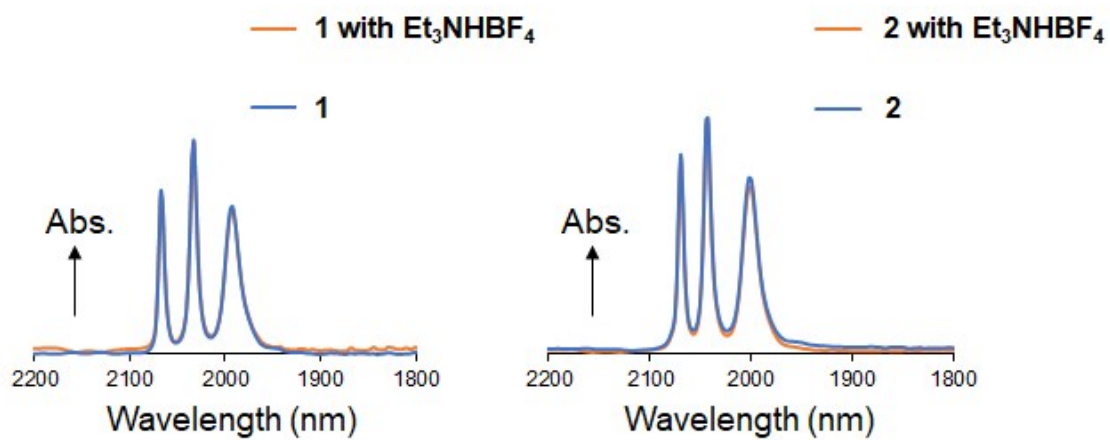


Figure S1. (left) IR spectra of **1** (1 mM) and **1** (1 mM) with 25 mM  $\text{Et}_3\text{NHBF}_4$  and 0.1 M  $\text{nBu}_4\text{NPF}_6$  in  $\text{CH}_2\text{Cl}_2$  solution, and (right) **2** (1 mM) and **2** (1 mM) with 25 mM  $\text{Et}_3\text{NHBF}_4$  and 0.1 M  $\text{nBu}_4\text{NPF}_6$  in  $\text{CH}_2\text{Cl}_2$  solution.

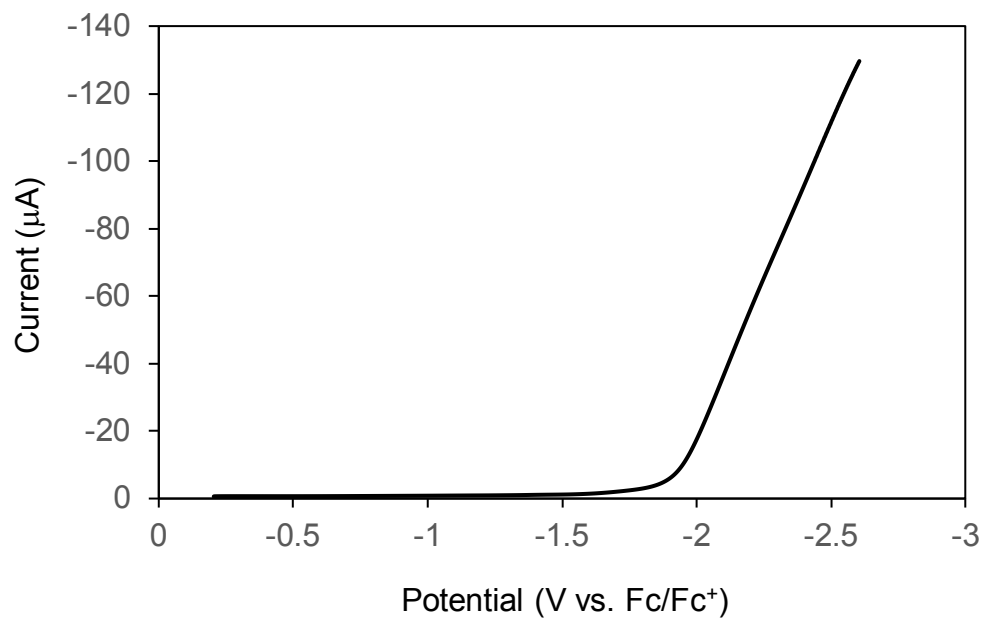


Figure S2. Cyclic voltammetry of 25 mM  $\text{Et}_3\text{NHBF}_4$  in  $\text{CH}_2\text{Cl}_2$  solution with 0.1 M  $\text{nBu}_4\text{NPF}_6$  electrolyte.

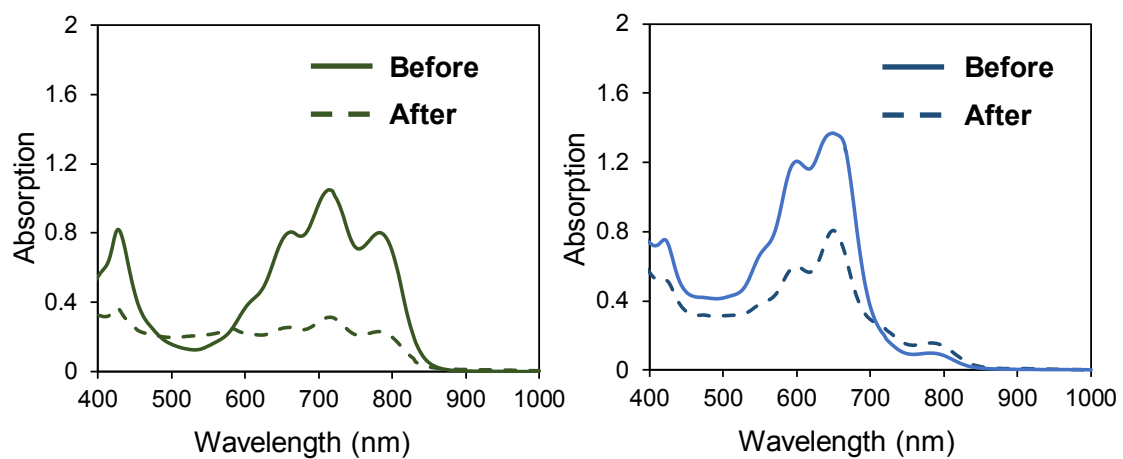


Figure S3. Absorption spectra of before and after bulk electrolysis of complexes (1 mM) with 25 mM  $\text{Et}_3\text{NHBF}_4$  and 0.1 M  $\text{nBu}_4\text{NPF}_6$  in  $\text{CH}_2\text{Cl}_2$  solution. (left) **1**, and (right) **2**.

Table S1. Summary of crystallographic data and refinement details of **1** and **2**

	<b>1</b>	<b>2</b>
Empirical formula	$C_{27}H_{11}Fe_2O_6S_4$	$C_{30}H_8Fe_4O_{12}S_4$
Mw	671.31	912.01
Crystal color and Habit	Green, Prism	Blue, Platelet
Crystal size [mm]	0.20 x 0.16 x 0.04	0.20 x 0.20 x 0.20
Crystal system	Monoclinic	Monoclinic
Space group	C2/c (#15)	C2 <sub>1</sub> /c (#14)
Temperature [oC]	-150	-150
a [Å]	36.212(12)	12.232(5)
b [Å]	7.359(2)	9.726(4)
c [Å]	21.219(7)	13.980(5)
β [o]	113.185(6)	107.386(9)
V [Å <sup>3</sup> ]	5198(3)	15187.1(11)
Z	8	2
Dcalc [g/cm <sup>2</sup> ]	1.716	1.908
F (000)	2696.00	904.00
μ [cm <sup>-1</sup> ]	14.793	21.186
2θmax	55.0	55.0
No. of reflections	23234	9852
Measured	5924	3560
Rint	0.0491	0.0425
No. of observations	5924	3560
No of parameters	379	226
R1 [ >2σ(I)]	0.0444	0.0465
wR2 [all data]	0.1043	0.0926
GOF	1.194	1.129