Supporting Information

A proton-hydride diiron complex with a base-containing diphosphine ligand relevant to the [FeFe]-hydrogenase active site†

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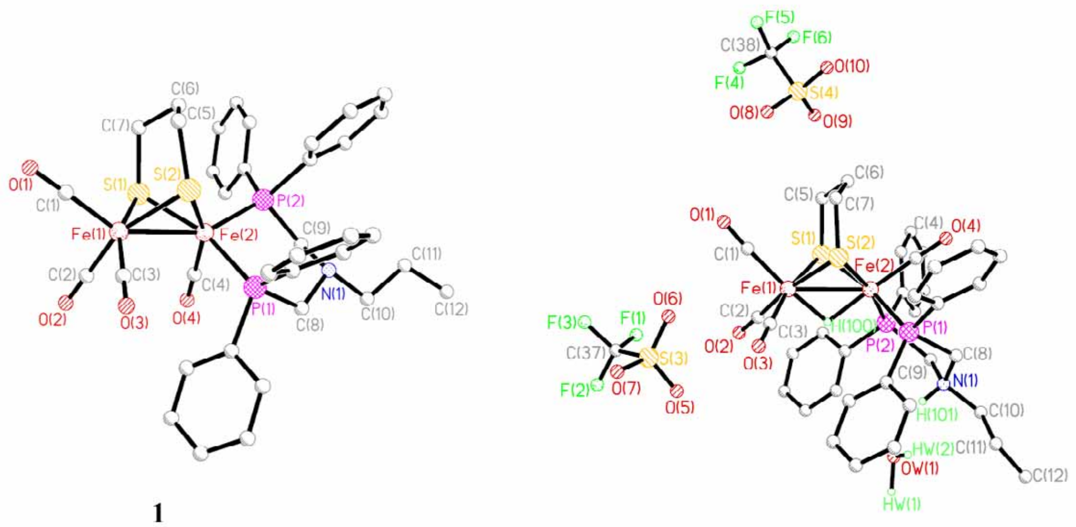
Preparation of 1 and [1(H_NH_μ)]$(OTf)_2$

[(μ-pdt){$Fe(CO)_3$}{Fe(CO)(κ^2-PNP)}] (1). Ligand Ph_2PCH_2N(*n*-Bu)CH_2PPh_2 (0.47 g, 1.0 mmol) was added to the toluene solution (20 mL) of [(*μ*-PDT)$Fe_2(CO)_6$] (0.39 g, 1.0 mmol). The red solution was refluxed for 3 h and the color turned dark red. The solvent was removed under reduced pressure. The residue was washed several times with hexane/CH_2Cl_2 (5:1, v/v). Then it was purified by chromatography on a silica gel column with hexane/CH_2Cl_2 (3:1, v/v) as eluent. A brown powder was obtained as complex **1** from the collected yellow band after removal of solvent. Yield: 0.68 g (86%). Single crystals suitable for X-ray analysis were recrystallized from hexane/CH_2Cl_2. Anal. Calc. for $C_{36}H_{37}Fe_2NO_4P_2S_2$: C, 55.05; H, 4.75; N, 1.78. Found: C, 55.05; H, 4.73; N, 1.85. ^1H NMR (400 MHz, $CDCl_3$): δ 7.21–7.71 (m, 20 H, 4 Ph), 3.76 (s, 2 H, PCH_2) 3.28 (s, 2 H, PCH_2), 2.44 (s, 2 H, NCH_2C), 1.68 (s, 2 H, $SCCH_2CS$), 1.45 (s, 4 H, SCH_2), 1.30 (s, 2 H, NCC*H*), 0.60 (s, 3 H, CCH_3). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ 52.5 (PNP). IR (CH_2Cl_2): ν_{CO} 2020, 1948, 1894 cm^{-1}. ESI-MS: *m/z* 786.1 $[M+H]^+$.

[(μ-H)(μ-pdt){$Fe(CO)_3$}{Fe(CO)(κ^2-PNHP)}]$(OTf)_2$ ([1(H_NH_μ)]$(OTf)_2$). Three equiv. of HOTf was added to a solution of **1** (0.79 g, 1.0 mmol) in diethyl ether (100 mL). The yellow solution was stirred for 5 min. A purple powder was deposited from the solvent and washed several times with diethyl ether. Yield: 0.95 g (88%). Single crystals suitable for X-ray analysis of [**1**(H_NH_μ)]$(OTf)_2$ were recrystallized from hexane/CH_2Cl_2. Anal. Calc. for $C_{38}H_{41}F_6Fe_2NO_{11}P_2S_4$: C, 41.36; H, 3.74; N, 1.27. Found: C, 41.30; H, 3.78; N, 1.24. ^1H NMR (400 MHz, d_6-acetone): δ 10.1 (br, 1 H, N*H*), 7.21–7.71 (m, 20 H, 4 Ph), 5.47–4.95 (m, 4 H, PCH_2), 3.97–3.76 (m, 2 H, NCH_2C), 3.28–1.88 (m, 8 H, $SCH_2CH_2CH_2S$, $NCCH_2$), 0.98 (s, 3 H, CCH_3), −13.6 (t, μ*H*, J_{H-P} = 20 Hz, H_N-exo), −13.9 (t, μ*H*, J_{H-P} = 20 Hz, H_N-endo). ^{31}P NMR (d_6-acetone): δ 46.2, 45.1 (PNP). IR (CH_2Cl_2): ν_{CO} 2105, 2057, 2043, 1990 cm^{-1}.



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[**1**(H_NH_μ)]$(OTf)_2 \cdot H_2O$

Fig. S1 Molecular structures of **1** (left) and [**1**(H_NH_μ)]$(OTf)_2 \cdot H_2O$ (right) as ball and stick drawings. Selected distances (Å) and angles (°) for **1**: Fe–Fe, 2.5565(7); Fe–S, 2.2527(10)–2.2644(11); Fe–P, 2.1981(10)–2.2132(11); Fe(1)–C, 1.786(5)–1.790(4); Fe(2)–C, 1.747(4); N–C, 1.456(5)–1.465(5); P(1)–Fe–P(2), 92.51(4); for [**1**(H_NH_μ)]$^{2+}$: Fe–Fe, 2.6120(16); Fe–S, 2.2493(16)–2.2593(16); Fe–P, 2.2185(17)–2.2319(15); Fe–H, 1.65(4)–1.70(3); Fe(1)–C, 1.799(6)–1.816(6); Fe(2)–C, 1.740(5); N–H, 0.90(3); N–C, 1.485(5)–1.509(5); P(1)–Fe–P(2), 95.82(6); Fe(1)–H–Fe(2), 102.8.

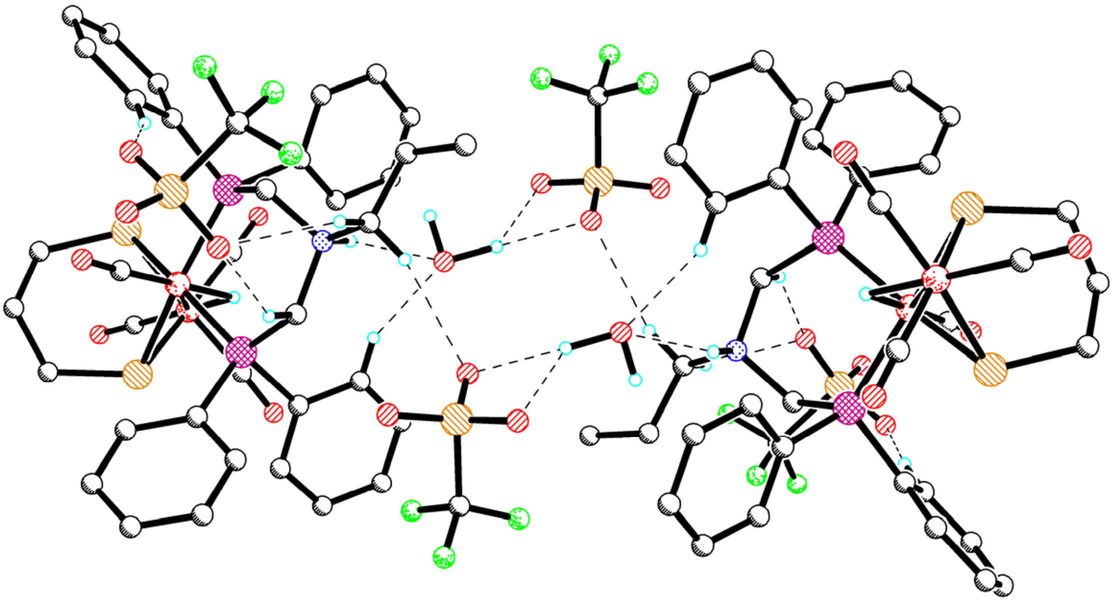

Fig. S2 Packing diagram showing the hydrogen bonds in two asymmetric units containing two molecules of [**1**(H_NH_μ)]$(OTf)_2$ and two molecules of H_2O. Hydrogen atoms, which are not involved in the hydrogen bonds, are omitted for clarity.

Table S1 Geometric parameters for the hydrogen bonds in the packing diagrams of complex [**1**(H_NH_μ)]$(OTf)_2$

D–H···A	D–H	H···A	D···A	D–H···A
N(1)–H(101)···O(w1)	0.889	2.022	2.805	146.32
O(w1)–H(w1)···O(5B)	1.103	1.921	2.831	137.10
O(w1)–H(w1)···O(7B)	1.103	2.158	3.102	141.96
C(9)–H(9a)···O(10)	0.970	2.524	3.380	147.1
C(10)–H(10b)···O(10B)	0.970	2.466	3.322	147.1
C(18)–H(18)···O(9B)	0.930	2.381	3.256	156.8
C(36)–H(36)···O(w1)	0.930	2.275	3.134	153.3

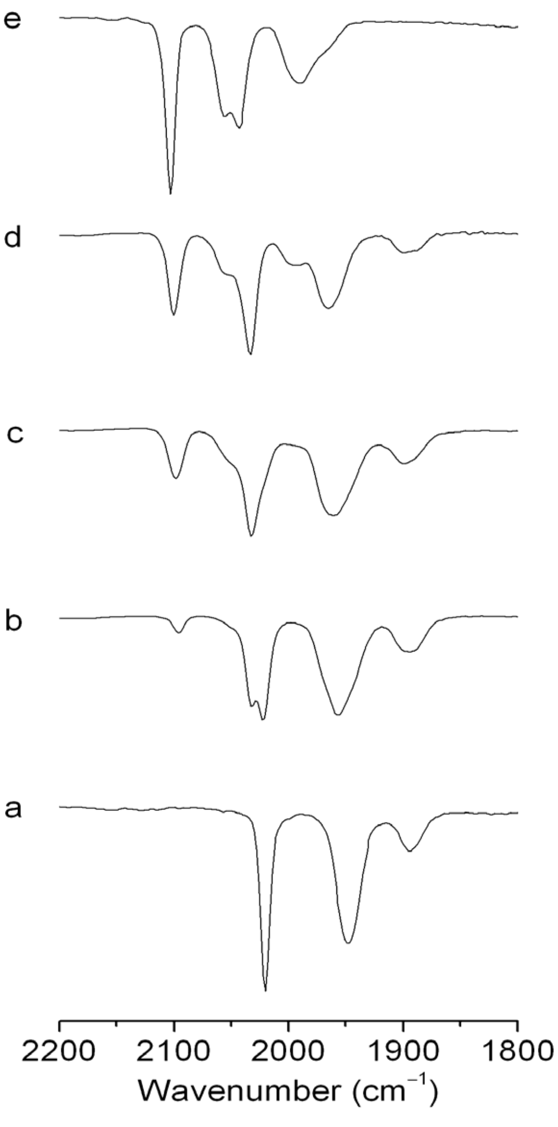

Fig. S3 Selected region of the IR spectra of **1** in $CHCl_3$ with (a) + 0 equiv., (b) + 0.5 equiv., (c) + 1.5 equiv., (d) + 2.5 equiv. and (e) + 3.5 equiv. HOTf.

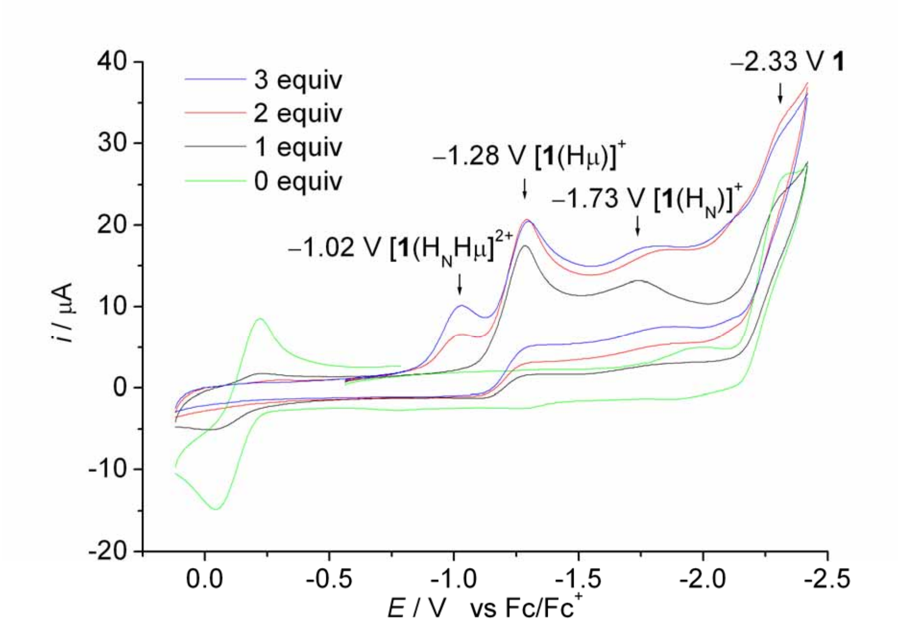

Fig. S4 Cyclic voltammograms of **1** (1.0 mM) in the presence of 0-3 equiv. of HOTf.