**Electronic Supplementary Information** 

# Homogeneous vs. heterogeneous catalysis for hydrogen evolution by a nickel(II) bis(diphosphine) complex

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## S1. Synthesis and characterization



**Figure S1.** <sup>1</sup>H-NMR spectrum (bottom) and <sup>31</sup>P-NMR spectrum (top right) of ligand  $P_2^{Ph}N_2^{PhCH_2COOH}$  in DMSO-d<sup>6</sup>.



Figure S2. Diffuse reflectance IR spectrum of ligand P<sub>2</sub><sup>Ph</sup>N<sub>2</sub><sup>PhCH<sub>2</sub>COOH</sup> in a KBr pellet.



Figure S3. <sup>1</sup>H-NMR spectrum (bottom) and <sup>31</sup>P-NMR spectrum (top right) of 1 in ACN-d<sup>3</sup>.



Figure S4. Diffuse reflectance IR spectrum of 1 in a KBr pellet.



Figure S5. Absorption spectrum of 1 in acetonitrile solution.



**Figure S6.** Cyclic voltammetry of 1 mM **1** in acetonitrile (0.1 M TBAPF<sub>6</sub> as supporting electrolyte), scan rate v = 100 mV/s.

#### S2. Electrocatalysis in acetonitrile



**Figure S7.** Comparison of the theoretical amount of hydrogen produced according to the charge passed (black trace) and the experimental amount determined by gas chromatography (red dots) during a 2-hour bulk electrolysis at -1.20 V vs. Fc/Fc<sup>+</sup> of a 1 mM acetonitrile solution of **1** containing 0.5 M TFA. A Faradaic efficiency of 77% can be estimated.

#### S2.1 Kinetics of electrocatalytic hydrogen formation in acetonitrile with TFA

Foot-of-the-wave analysis (FOWA)<sup>[S1]</sup> was applied to estimate the kinetics of the first protonation step ( $k_1$  in Figure 1B of the main text). An average value was obtained from the FOWA of the CV response of 1 mM **1** in acetonitrile in the presence of 0.3, 0.4, and 0.5 M TFA at a scan rate of v = 100 mV/s, according to eq S1, where  $c_{TFA}$  is the concentration of acid, f = F/RT.

$$\frac{i_{cat}}{i_p} = \frac{4.48 \sqrt{\frac{k_1 C_{TFA} RT}{F v}}}{1 + \exp\left[f(E - E_{cat})\right]}$$
(S1)

The rate constant of the second protonation ( $k_2$  in Figure 1B of the main text) was estimated from the potential shift of the catalytic wave according to eq S2.

$$E_{cat} = E_{Ni(I)/Ni(0)} + \frac{RT}{F} ln \left( 1 + \sqrt{\frac{k_1}{k_2}} \right)$$
(S2)



**Figure S8.** Foot-of-the-wave analysis (FOWA) of the CV response of 1 mM **1** in acetonitrile solution in the presence of 0.3 (top), 0.4 (middle), and 0.5 M (bottom) TFA.

Tafel plot analysis was then performed to benchmark electrocatalysis by complex 1 in acetonitrile using TFA as the proton source. For an EECC catalytic mechanism with  $k_1 \gg k_2$ , the TOF<sub>max</sub> can be calculated according to eq S3, with c<sub>TFA</sub> set to the reference value of 1 M.<sup>[S2]</sup>

$$TOF_{max} = k_2 c_{TFA} \tag{S3}$$

The TOF- $\eta$  relationship (Tafel plot, Figure 2 blue line) can be then obtained upon application of eq S4, with  $E_{TFA}^{0}$  being the thermodynamic potential for the reduction of TFA in acetonitrile (-0.61 V vs. Fc/Fc<sup>+</sup>).<sup>[S3]</sup>

$$TOF = \frac{TOF_{max}}{1 + exp[f(E_{TFA}^{0} - E_{cat})]exp(-f\eta)}$$
(S4)

### S3. Photocatalysis in aqueous solution



**Figure S9.** Kinetics of photoinduced hydrogen evolution from 5 mL aqueous solutions containing 50  $\mu$ M **1**, 0.5 mM Ru(bpy)<sub>3</sub><sup>2+</sup>, and 0.5 M ascorbic acid in the range of pH 3-6.



**Figure S10.** Luminescence spectra (excitation at 480 nm) of aqueous solutions containing 0.07 mM  $Ru(bpy)_3^{2+}$  and 0-150  $\mu$ M **1**.



**Figure S11.** Luminescence spectra (excitation at 480 nm) of aqueous solutions containing 0.07 mM  $Ru(bpy)_3^{2+}$  and 0-0.5 M ascorbic acid at pH 5.



**Figure S12.** Initial rates of photoinduced hydrogen evolution from 5 mL aqueous solutions containing 0-150  $\mu$ M **1**, 0.5 mM Ru(bpy)<sub>3</sub><sup>2+</sup>, and 0.5 M ascorbic acid at pH 5.

#### S3.1 Photocatalytic hydrogen evolution

Results from photochemical hydrogen evolution by **1** in the presence of  $Ru(bpy)_3^{2+}$  as the sensitizer and ascorbic acid as the sacrificial donor (Figure 3A) have been analyzed to extract relevant parameters such as maximum turnover number (TON) and turnover frequency (TOF, min<sup>-1</sup>).

Maximum TONs have been estimated according to eq S5 using the amount of hydrogen in moles ( $n_{H_2}$ ) attained at the plateau of the kinetic traces in Figure 3A and the initial amount of catalyst in solution ( $n_1$ ).

$$TON = \frac{n_{H_2}}{n_1} \tag{S5}$$

Maximum TOFs have been estimated according to eq S6, in which the hydrogen production rate ( $R_{H_2}$ ) has been calculated from the fitting of the hydrogen evolution kinetics (Figure 3A) in the linear portion of the traces (typically between 0.5-2 hours irradiation).

$$TOF = \frac{R_{H_2}}{n_1} \tag{S6}$$

The data obtained are collected in Table S1 and in Figure 3B in a pictorial representation.

[1] (µM)	$n_{ m H_2}$ (µmol)	R <sub>H2</sub> (μmol min <sup>-1</sup> )	TON	TOF (min <sup>-1</sup> )
10	18.2	0.057	272	1.14
25	20.1	0.069	146	0.55
50	21.8	0.107	80	0.43
100	25.3	0.127	43	0.25
150	13.6	0.084	33	0.11

Table S1. Photocatalytic data from Figure 3A.

### S4. Characterization of 1@TiO<sub>2</sub>



Figure S13. Full range diffuse reflectance FT-IR spectrum obtained on 1@TiO<sub>2</sub> in KBr pellet.



Figure S14. Absorption spectrum of the aqueous solution obtained upon treatment of 1@ TiO<sub>2</sub> (1 cm<sup>2</sup> surface area) with 8 mL 0.1 M NaOH (optical pathlength of 0.1 cm); a molar extinction coefficient of  $\varepsilon = 53,000$  M<sup>-1</sup>cm<sup>-1</sup> at 257 nm was used as obtained with complex 1 in 0.1 M NaOH.



**Figure S15.** J-V curves of bare  $TiO_2$  and **1@TiO\_2** in 0.1 M Na<sub>2</sub>SO<sub>4</sub> (scan rate v = 100 mV/s) at pH 2 (top) and pH 4 (bottom).

### **S5.** References of the ESI

- [S1] C. Costentin, S. Drouet, M. Robert and J. M. Saveant, J. Am. Chem. Soc., 2012, 134, 11235.
- [S2] C. Costentin and J. M. Saveant, ChemElectroChem, 2014, 1, 1226.
- [S3] V. Fourmond, P.-A. Jacques, M. Fontecave and V. Artero, *Inorg. Chem.*, 2010, 49, 10338.