Electronic Supplementary Information (ESI) for *Chem. Comm*.

A square-planar nickel dithiolate complex as an efficient molecular catalyst for the electro- and photoreduction of protons

Geng-Geng Luo,[a,*†] Yong-Heng Wang,[b,†] Jiang-Hai Wang,[a] Ji-Huai Wu[a] and Rui-Bo Wu[b]

[a] College of Materials Science and Engineering, Huaqiao University, Xiamen 361021, P. R. China

[b] School of Pharmaceutical Sciences, East Campus, Sun Yat-sen University, Guangzhou 510006, P. R. China

***E-mail*:** ggluo@hqu.edu.cn Fax: +86-592-6162225

Table of Contents

1. Materials and Syntheses.....S2

2. Instrumentation.....S3

3. Electrochemical Experiments.....S3

4. Photochemical Experiments.....S4

5. Computational Details.....S4

6. References.....S5

7. Examples of Square-Planar NiN_2S_2 Complexes.....S6

8. XRD, ESI-MS and UV-vis Analysis.....S7

9. Electrochemical Studies.....S9-S12

10. Photochemical Studies.....S13-S15

11. DFT Calculations.....S16-S25

Electronic Supplementary Information (ESI)

1. Materials and Syntheses

All chemicals and reagents were purchased from Sigma-Aldrich unless noted. Water (18.2 MΩ) was purified using Milli-Q system. All solvents were dried and distilled using common techniques unless otherwise mentioned. All reactions are carried out under a N_2-atmosphere.

Synthesis of ligand L (N,N'-dimethyl-N-N'-bis(2-mecaptoethyl)-ethylenediaminato). The synthesis of the ligand L was synthesized by modification of published procedures.[1] A solution of N,N-dimethyl-1,3-ethanediamine(4.6861g, 53.16 mmol) in 5 mL benzene was placed in Schlenk reaction tube and the temperature was raised to 40ºC. Propylene sulfide (8.2 mL, 111.64 mmol) in 5 mL benzene was then added dropwise, the temperature was raised to 80ºC. The mixture was stirred overnight at 80 ºC. The oily product was washed with 4x 10 mL of distilled water in a 125 mL separatory funnel. The ligand L solution was then dried over $MgSO_4$ and gravity filtered into a tarred 25 mL round-bottom flask. The benzene was removed to yield a colorless viscous liquid (6.7577g, 24.13 mmol, 45.4% yield). ^{1}H NMR (500 MHz, d^6-DMSO): δ (ppm) = 2.4-2.8 (m, 8H), 2.2 (s, 6H), 2.1 (s, 2H).

Synthesis of complex 1 (N,N'-dimethyl-N-N'-bis(2-mecaptoethyl)-ethylene diaminato) nickel(II). The neutral nickel(II) complex **1** was synthesized with published procedures.[2,3] A solution of $Ni(OAc)_2{\cdot}4H_2O$ (2.494 g, 0.010 mol) was prepared in 70 mL of a 1 : 1 MeOH/EtOH solvent mix. The solution was then added to a solution of L (2.084 g, 0.010 mol) in 60 mL of ethanol. The resulting solution immediately became red/brown in color. It was stirred under an inert atmosphere overnight, filtered, and then the solvent volume reduced under vacuum to about 70 mL, and filtered again. Approximately 20 mL of diethyl ether was added, and the solution was left at low temperature for three days, resulting in reddish precipitation of **1**. Yield = 2.067g (78%). Anal. Calcd (found) for $NiC_8H_{18}N_2S_2$: C, 36.25(35.35); H, 6.85 (6.61); N, 10.57 (9.92). MS (ESI, m/z): $[M]^+$ calcd. For $NiC_8H_{18}N_2S_2$, 265.06; found 265.04. ^{1}H NMR (500 MHz, d^6-DMSO): δ (ppm) = 3.27 (m, 2H), 3.03 (m, 2H), 2.75 (s, 6H), 2.50 (m, 4H), 2.33 (m, 2H), 2.28(m, 2H). Single crystals suitable for X-ray diffraction were grown through the diffusion of diethyl ether into an ethanol solution of **1**.

Synthesis of complex ZnN_2S_2 (N,N'-dimethyl-N-N'-bis(2-mecaptoethyl)-ethylene diaminato) zinc(II). The synthesis of Zn(II) complex (ZnN_2S_2) was synthesized using literature methods.[4] A solution of NaH (0.52 g, 22 mmol) in ethanol was added to an ethanol solution of L (2.25 g, 10.8 mmol) under Ar. The mixture was stirred at room temperature for 1h, and then an ethanolic solution of $ZnCl_2$ (1.47 g, 10.8 mmol) was added. The resulting cloudy mixture was stirred for 48 h. The solution was evaporated to dryness under reduced pressure, and the resulting

white solid was washed first with water and then diethyl ether. Remaining sodium salts were removed by dissolution of the crude product into dichloromethane and extraction with water. Evaporation of CH_2Cl_2 layer yielded a crude product that was washed with diethyl ether (0.876 g, 30%). The product was recrystallized from CH_2Cl_2/diethyl ether solution with yield of 35%. Anal. Calcd (found) for $ZnC_8H_{18}N_2S_2$: C, 35.35(35.25); H, 6.67 (6.48); N, 10.31 (10.15). ^{1}H NMR (500 MHz, $CDCl_3$-d^6): δ (ppm) = 2.87 (m, 2H), 2.87 (m, 2H), 2.63 (m, 2H), 2.61 (s, 6H), 2.52 (m, 2H), 2.50 (m, 2H).

2. Instrumentation

UV-vis absorption spectra were recorded on a UV-2100 (Shimadzu) spectrophotometer. Steady-state fluorescence spectroscopic studies in solution were performed on a ThermoFisher spectrophotometer with a xenon arc lamp as light source. Samples for absorption and emission measurements were contained in 1cm×1cm quartz cuvettes. C, H and N microanalyses were carried out with a CE instruments EA 1110 analyzer. The ^{1}H NMR were recorded on a Bruker AVANCE III 500 MHz spectrometer with tetramethylsilane (TMS, 0.00 ppm) as an internal standard and d_6-DMSO (or d_6-$CDCl_3$) as solvent. Coupling constants (J) values are given in Hz. Mass spectrometry (MS) experiment was carried out in the positive ion made on a Bruker Esquire HCT ion trap mass spectrometer (Billerica, MA) coupled with a homemade electrospray ionization (ESI) device. Parameters of the ESI source were optimized to enhance the signal intensity. The pressure of nebulizing nitrogen, the flow rate of desolvation gas, and the temperature of desolvation gas were set to 8 psi, 1L/min, and 250 ºC, respectively. The experimental powder X-ray diffraction (PXRD) was measured on a Panalytical X-Pert Pro diffractometer with Cu Kα radiation equipped with an X'Celerator detector. X-ray single crystal diffraction measurement was done on a Rigaku R-AXIS RAPID Image Plate single-crystal diffractometer. SHELXS-97 and SHELXL-97 were used to solve and refine the crystal structure.

3. Electrochemical Experiments

Cyclic voltammogram was conducted on an electrochemical workstation (CHI 650E) using a three-electrode single-compartment cell (glassy carbon working electrode, Pt wire auxiliary electrode and saturated calomel reference electrode) at room temperature. All measurements were performed in acetonitrile (MeCN) in the presence of 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) as a supporting electrolyte. Measurements were made using optically dilute solutions after deoxygenation by purging with dried N_2. Ferrocene was added to each sample solution at the end of the experiments, and the ferrocenium/ferrocene (F_c/F_c^+) redox couple was used as an internal potential reference.

Electrochemical experiment in the presence of acetic acid: Under nitrogen atmosphere, **1** was dissolved in degassed MeCN, 0.1 M TBAP solution. Acetic acid was added to the red solution of the complex. After the addition of the acetic acid solution a cyclic voltammogram was recorded. The addition was repeated several times to increase the concentration of acetic acid. After every addition a cyclic voltammogram was recorded. GC-2014C-TCD with molecular sieve column was used for product detection.

4. Photochemical Experiments

For photoinduced hydrogen evolution, solutions of FL (1 mM), TEA (0.36 M), Nickel catalyst **1** were prepared in pure water, giving a total volume of 10.0 mL. The solution was sealed with a septum, degassed under vacuum and flushed with Ar gas four times before irradiation. The cuvettes were irradiated by a Xenon Light Source with an optical filter employed to cut off light with wavelengths below 420 nm with constant stirring. The pH value of the solution was adjusted to the desired value using 4 M HCl as required and measured on OHAUS ST5000 pH meter. During irradiation, the headspace of the vials were analyzed by gas chromatography (GC) analysis (Shimadzu GC-2014C) with a thermal conductivity detector (TCD) and a Quadrex column and were quantified according to a calibration curve.

5. Computational Details

All calculations were carried out using the Gaussian 09 program.[5] The hybrid density functional (U)B3P86[6] was used in combination with the standard 6-311+G(d,p) basis set.[7] All structures were fully optimized in acetonitrile (MeCN) solvent (ε = 35.688) using the PCM method.[8] Vibrational analyses at the same level of theory were performed to confirm each stationary point to be either a local minimum or a transition state (TS), and to obtain thermal corrections.[9] The connection of each TS to its corresponding reactant and product was confirmed by *IRC* (intrinsic reaction coordinate) calculations.[10] Because thermal corrections based on the ideal gas phase model overestimate entropy contributions to free energies for reactions involving component change,[11] a relative free energy correction of 4.3 kcal mol^{-1} was added to the product state of H_2 release step.

Acetic acid was used as proton donor to calculate the free energy changes for protonation step through following equation:

$$B^- + AcOH \rightarrow BH + AcO^-,$$

where B is proton acceptor. Because the acetic acid was excessive to catalyst with a ratio of about 100:1, a correction of –2.7 kcal mol^{-1} was added to the standard free energy change of protonation step based on van't Hoff formula:

$$\Delta G = \Delta G^\circ + RT \cdot \ln Q,$$

where ΔG° is standard free energy change, R is mole gas constant, T is temperature and Q is reaction quotient.

The reduction potential was determined using isodesmic reaction[12] with the reduction of **1** to **2e** as the reference reaction (E°_{ref} = -1.92 V vs. SCE determined by experiment):

$$Ox + \mathbf{2e} \rightarrow Red + \mathbf{1},$$

where Ox and Red is oxidant and reductant respectively. The free energy change ΔG^o of this isodesimic reaction was used to calculate the reduction potential E^o of desired reaction using following formula:

$$E^\circ = -\Delta G^\circ / F + E^\circ_{ref},$$

where *F* is Faraday's constant.

6. References

[1] J. L. Corbin, K. F. Miller, N. Pariyadath, S. Wherland, A. E. Bruce, *Inorg. Chim. Acta.*, 1984, **90**, 41.

[2] D. Nakane, S. Kuwasako, M. Tsuge, M. Kubo, Y. Funahashi, T. Ozawa, T. Ogura and H. Masuda, *Chem. Commun*., 2010, **46**, 2142.

[3] P. V. Rao, S. Bhaduri, J. Jiang and R. H. Holm, *Inorg. Chem*., 2004, **43**, 5833.

[4] C. A. Grapperhaus, C. S. Mullins, P. M. Kozlowski and M. S. Mashuta, *Inorg. Chem*., 2004, **43**, 2859.

[5] A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010. *Gaussian09 Rev. B.01,* Gaussian, Inc., Wallingford CT, 2010.

[6] A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

[7] L. A. Curtiss, M. P. McGrath, J.-P. Blaudeau, N. E. Davis, R. C. Binning Jr. and L. Radom, *J. Chem. Phys*., 1995, **103**, 6104.

[8] G. Scalmani and M. J. Frisch, *J. Chem. Phys.*, 2010, **132**, 114110.

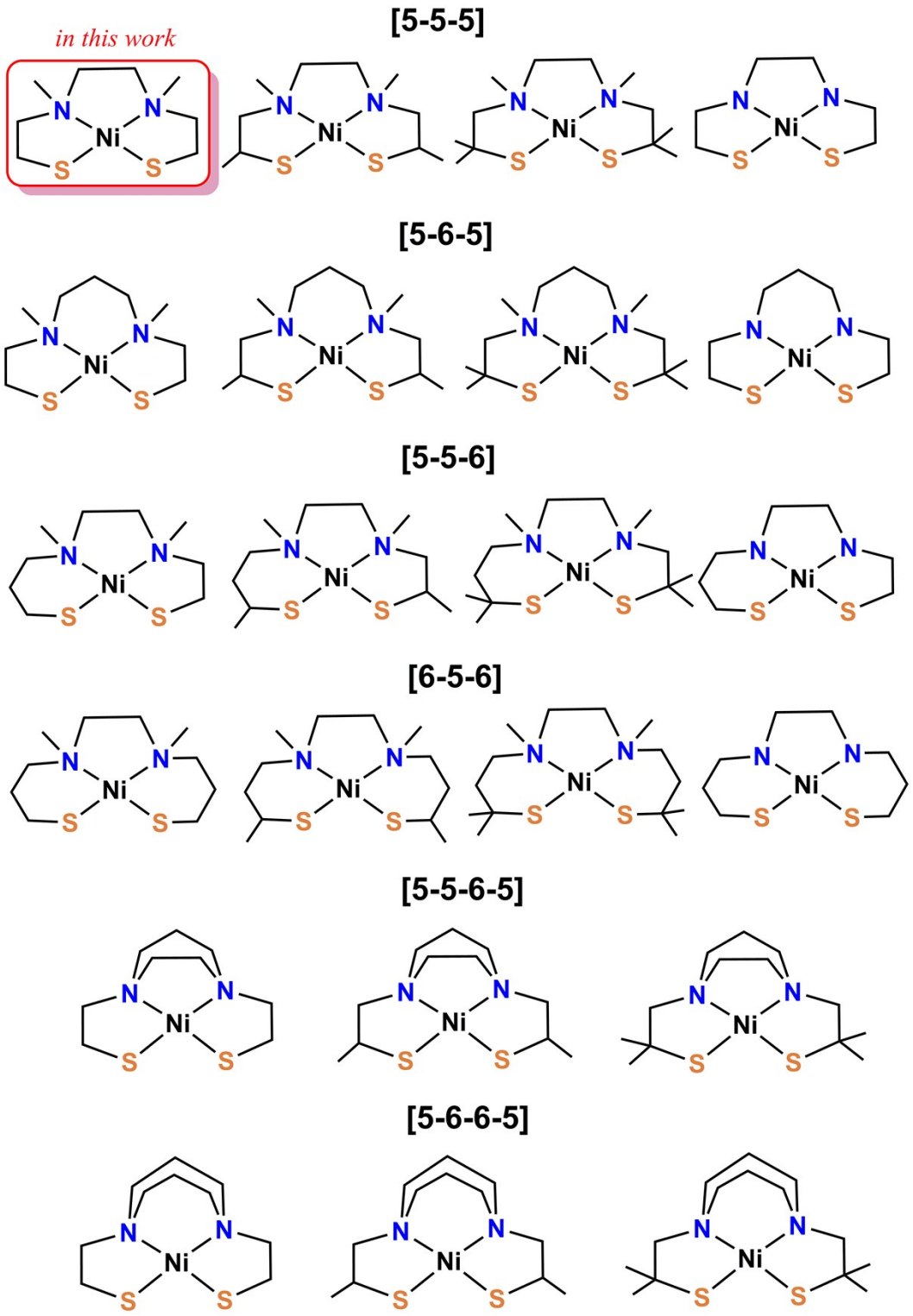
[9] R. F. Ribeiro, A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B,* 2011, **115**, 14556.

[10] C. Gonzalez and H. B. Schlegel, *J. Chem. Phys.*, 1989, **90**, 2154.

[11] S. Qu, H. Dai, Y. Dang, C. Song, Z.-X. Wang and H Guan, *ACS Catal.*, 2014, **4**, 4377.

[12] C. N. Virca and T. M. McCormick, *Dalton Trans.*, 2015, **44**, 14333.

7. Examples of Square-planar NiN_2S_2 Complexes



Scheme S1 Examples of the various chelate ring sizes observed in the square-planar NiN_2S_2 complexes. See Reference: *Chem. Rev*., 2015, **115**, 5248-5273.

8. XRD, ESI-MS and UV-vis Analysis

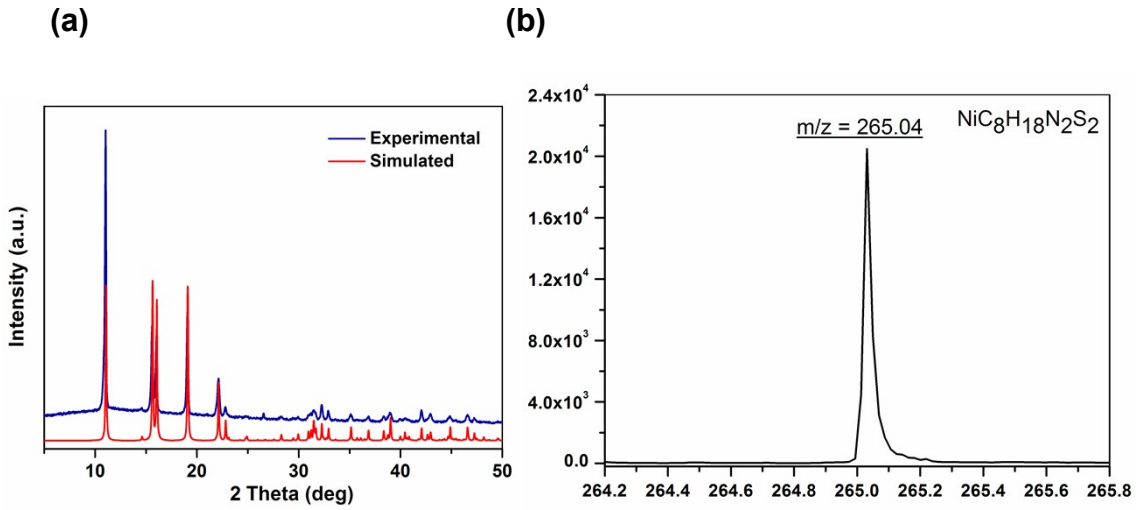


Fig. S1 (a) The simulated (red) and experimental (blue) PXRD patterns for complex **1**. (b) ESI-MS of **1**.

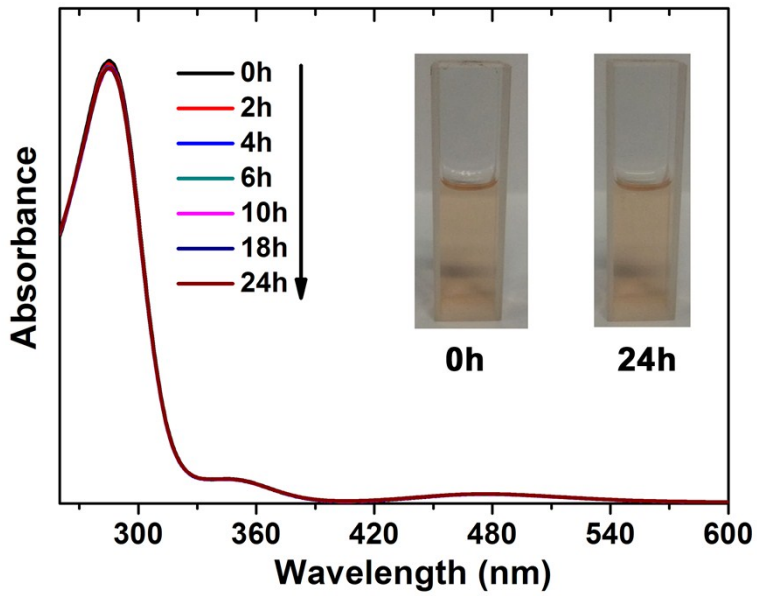


Fig. S2 Temporal evolution of UV-vis absorption spectra of **1** in air. Inset: the corresponding solution of **1** exposure to air after 0h and 24h.

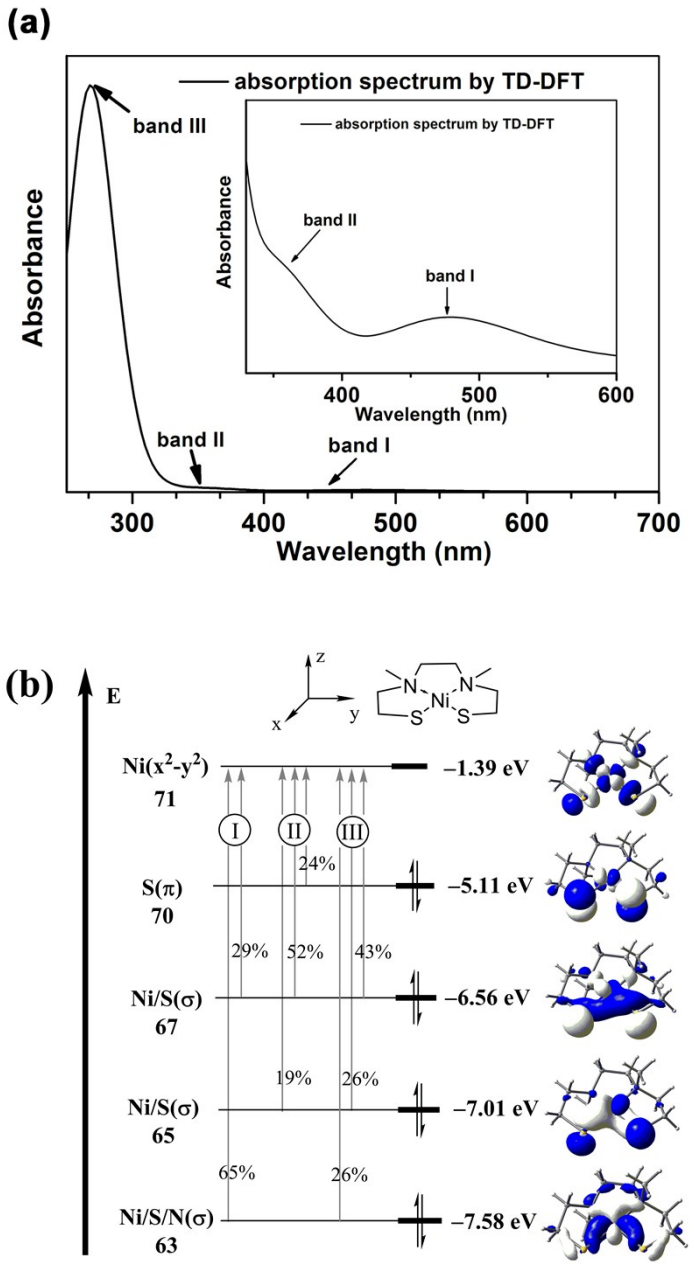


Fig. S3 (a) Absorption spectrum of **1** calculated by TD-DFT (PCM, EtOH). (b) Qualitative MO energy-level diagram and isosurface plots obtained from a DFT calculation for complex **1**. The one-electron excitations producing the major contributions to the transitions responsible for bands I-III (as provided by TD-DFT calculations) are also indicated.

9. Electrochemical Studies

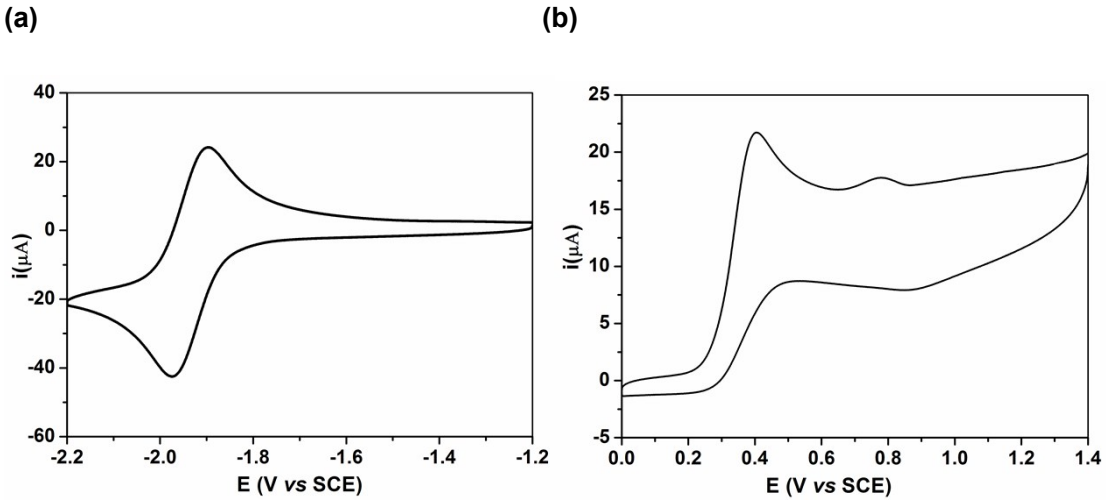


Fig. S4 Cyclic voltammogram of 1 mM of complex **1** recorded in 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) in MeCN. The system was scanned towards anodic potentials (a) and versus cathodic potentials (b). Scan rate of 200 mV s^{-1}; glassy carbon electrode.

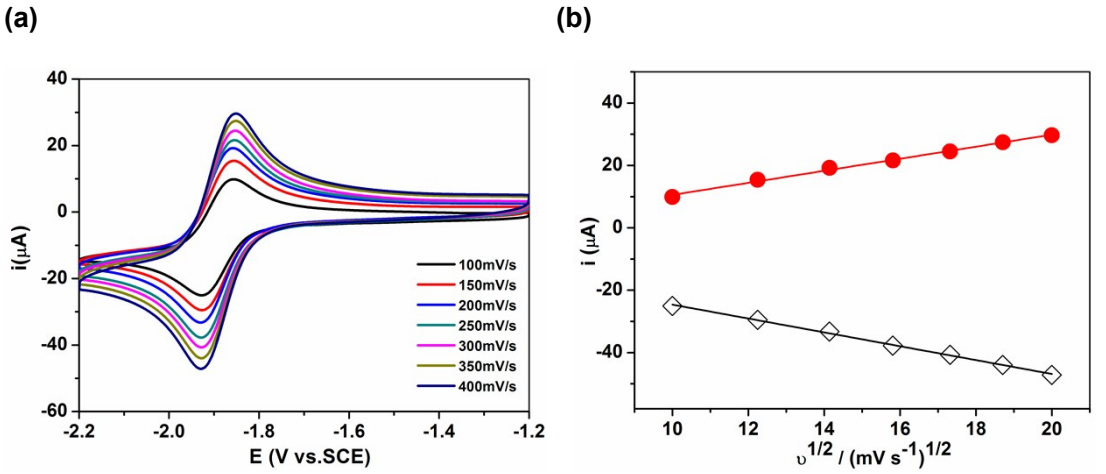


Fig. S5 (a) Cyclic voltammograms of 1 mM of complex **1** in 0.1 M n-Bu_4NPF_6 in MeCN under N_2 conditions with scan rate varied from 100 to 400 mV s^{-1}. (b) Peak currents vs. square root of scan rate. Room temperature conditions; glassy carbon electrode.

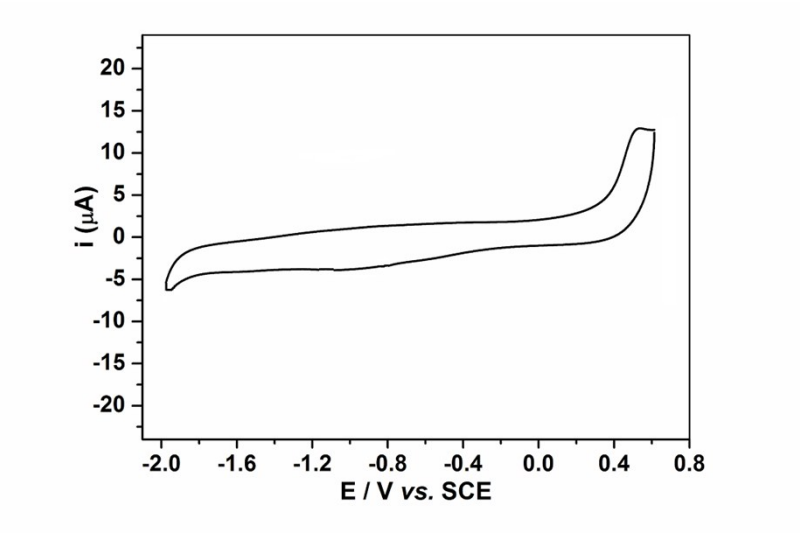


Fig. S6 Cyclic voltammogram of 0.8 mM of the complex ZnN_2S_2 recorded in 0.1 M tetrabutylammonium hexafluorophosphate (*n*-Bu_4NPF_6) in MeCN. Scan rate of 200 mV s^{-1}; glassy carbon electrode.

***Comments*:** Considering that the Zn(II) is redox inactive, one oxidation peak at 0.50 V is likely assigned to the ligand-centred oxidation, which indicates that the N_2S_2 ligand is non-innocently behavior.

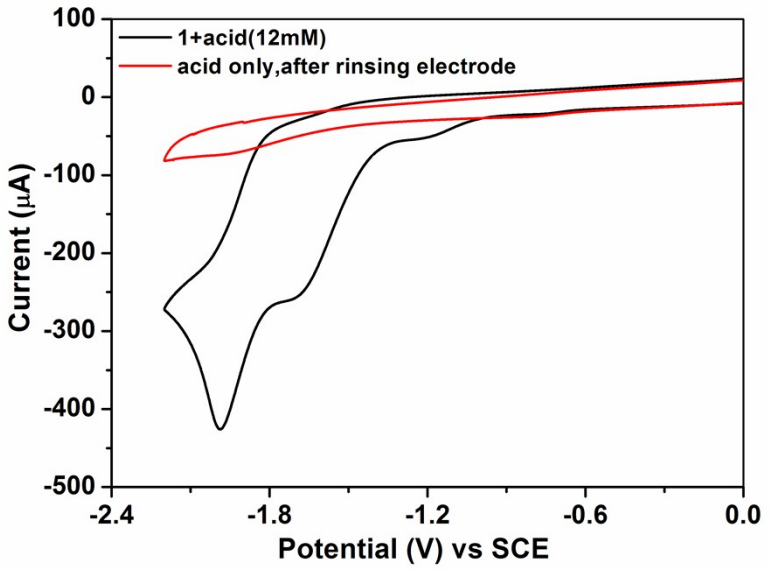


Fig. S7 Linear sweep voltammogram of 1 mM **1** in MeCN (0.1 M Bu_4NPF_6) with 12 mM acetic acid added (black) and a subsequent CV using the same electrode after rinsing and transfer to fresh in MeCN (0.1 M Bu_4NPF_6) without adding **1** with 12 mM acetic acid added (red). ν = 0.2 V/s vs Fc^+/Fc.

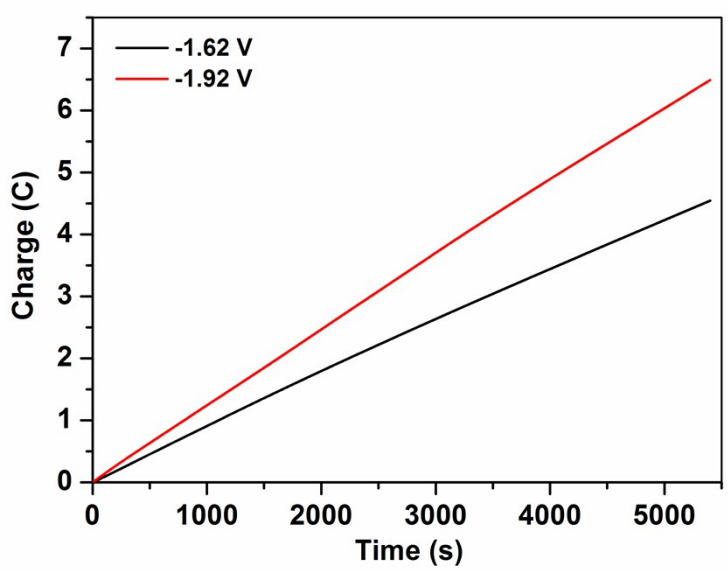


Fig. S8 Charge buildup of complex versus a series of applied potentials. All data have been deducted blank.

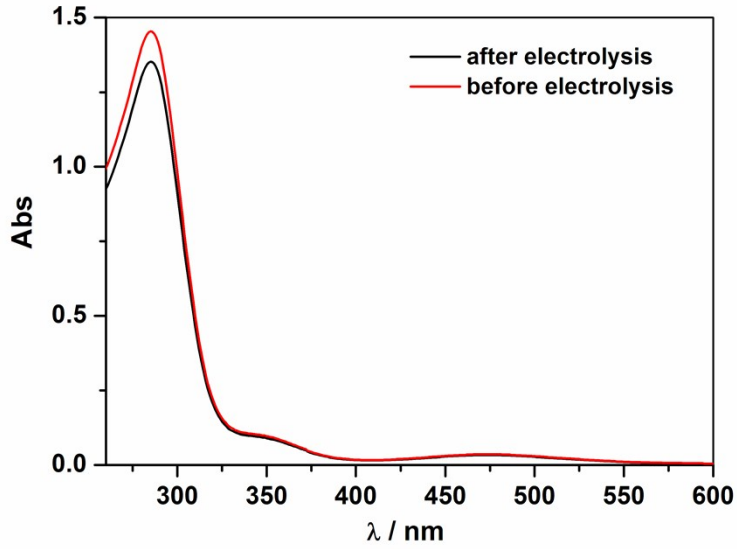


Fig. S9 The electronic absorption spectra of complex **1** before and after 1.5 h electrolysis.

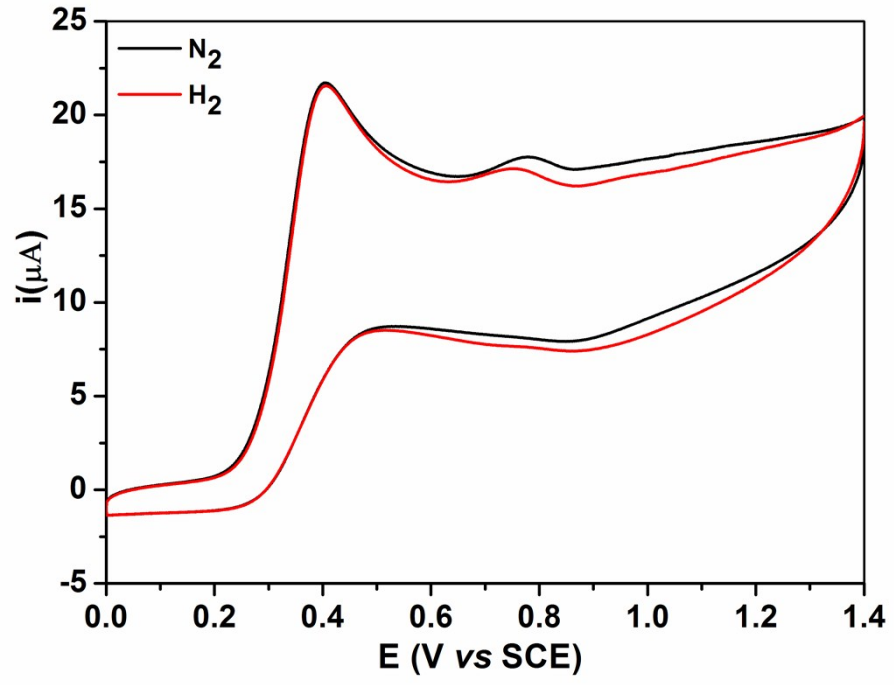


Fig. S10 Cyclic voltammograms of **1** in the presence and absence of hydrogen gas. The black line shows the voltammogram before exposure of the solution to H_2. The red line shows the voltammogram in a solution saturated with 1 atm of H_2 prepared by sparging immediately preceding measurement. The experimental conditions are 1 mM **1** in MeCN, 0.1 M $TBAPF_6$, and an electrochemical potential scan rate of 200 mV s^{-1}.

10. Photochemical Studies

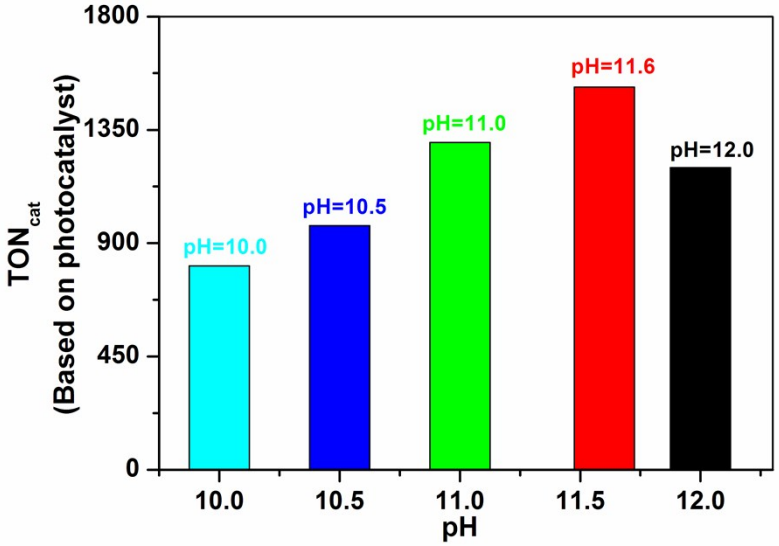


Fig. S11 Effect of pH value of the system on hydrogen evolution containing catalyst **1** (10 μM), FL (1 mM) and TEA (5% v/v) in H_2O over 24 h of Xe irradiation (λ > 420 nm).

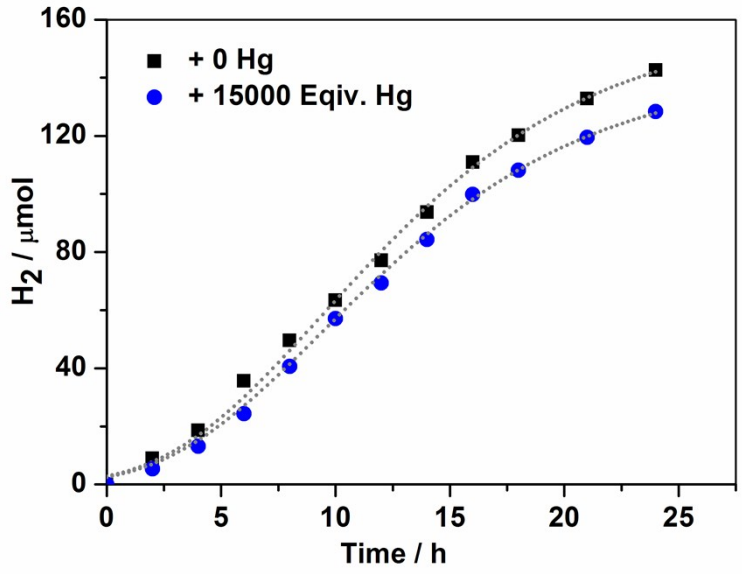


Fig. S12 Mercury poison experiment for the hydrogen generation by visible light irradiation (λ > 420 nm) of catalyst **1**, FL and TEA in H_2O at pH 11.6.

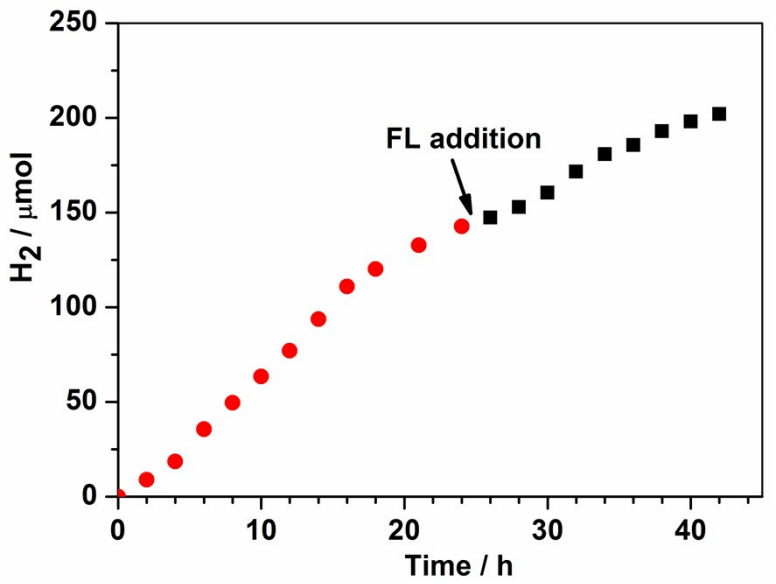


Fig. S13 Partial regeneration of catalytic activity upon the addition of one equivalent of FL in compositions containing 10 μM of **1** after 24 h of continuous illumination in the presence of 1 mM FL initially.

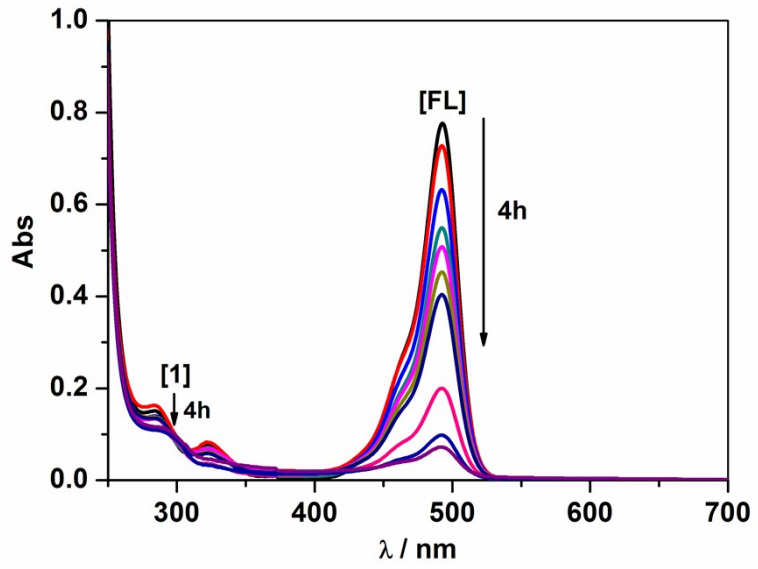


Fig. S14 UV-vis absorption spectra of photolysis systems containing catalyst **1** (20 μM), FL (10 μM) and TEA (5% v/v) in H_2O at pH 11.6 upon irradiation (λ > 420 nm).

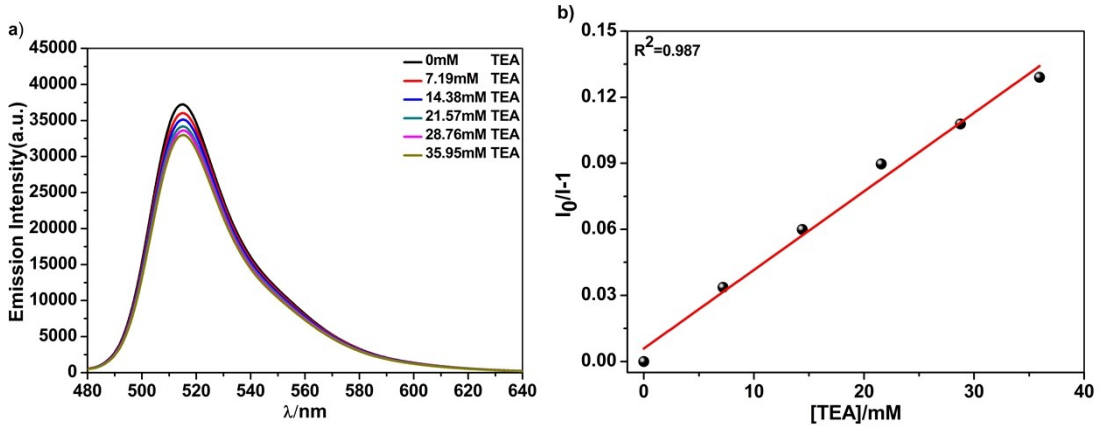


Fig. S15 a) Photoluminescence spectra of FL as a function of TEA. b) Stern-Volmer plot of quenching by TEA.

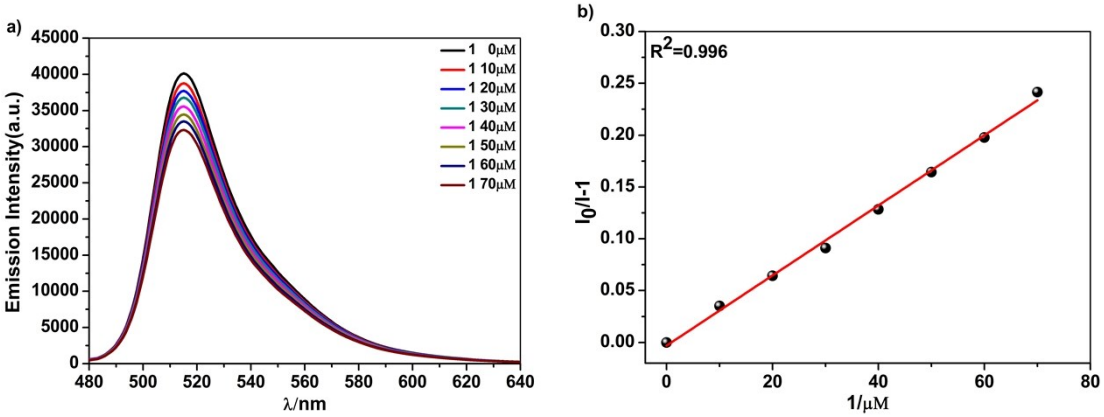


Fig. S16 a) Photoluminescence spectra of FL as a function of **1**. b) Stern-Volmer plot of quenching by **1** (inner filter correction applied).

***Comments*:** In photodriven catalytic systems, two electron transfer reaction pathways are possible. One is that the photoexcited FL^* might be oxidatively quenched by the WRC to generate $[FL]^{\bullet+}$. The other is that the photoexcited FL^* could be reductively quenched by the TEA to produce $[FL]^{\bullet-}$, which delivers an electron to the WRC for proton reduction to H_2. To determine the dominant reaction pathway in the system, the luminescence of the excited photosensitizer FL^*, in deaerated H_2O at pH 11.6 is undertaken as a function of both TEA and separately, **1** concentration (Fig. S15-S16, ESI‡). Stern-Volmer analyses yielded the quenching constants for the system. The rate constants for reductive quenching of FL^* by TEA and oxidative quenching by **1** are 2.6×10^7 and 9.8×10^9 M^{-1} s^{-1}, respectively. These results show that the quenching processes are diffusion controlled. Although the rate constant for oxidative quenching is about 400 times larger than that of reductive quenching, the reductive quenching process is still dominant given the much higher concentration of TEA (0.36 M) relative to **1** (10 μM). Due to the dominant reductive process, FL should bleach much more rapidly because of the instability of $[FL]^{\bullet-}$ formed, leading to the

deactivation of the photocatalytic system as mentioned above.

11. DFT Calculations

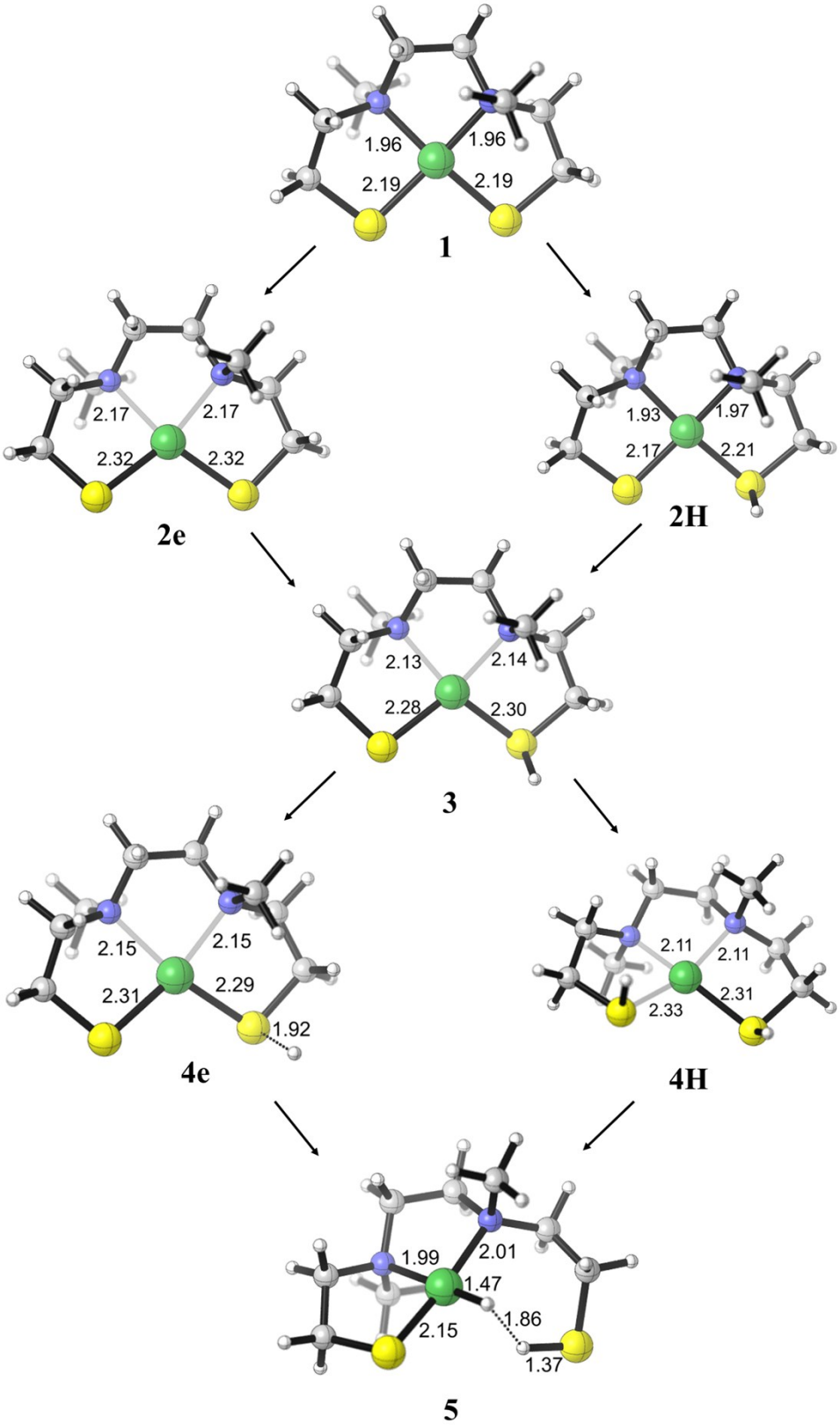


Fig. S17 DFT-computed electrocatalytic mechanism of hydrogen production.

Molecular Geometries and Energies

B3P86 (PCM, MeCN) Cartesian coordinates and energies in Hartree

AcOH

Number of imaginary freguencies: 0

Charge = 0, Multiplicity = 1

C	-1.386628000	-0.117718000	-0.000019000
H	-1.916086000	0.831577000	-0.001496000
H	-1.665950000	-0.701893000	-0.879247000
C	0.088040000	0.120230000	-0.000037000
O	0.631416000	1.200657000	0.000003000
O	0.782772000	-1.030179000	-0.000013000
H	-1.666154000	-0.699078000	0.881033000
H	1.726211000	-0.809502000	0.000128000

Energy (0K) = -229.738604

Energy (0K) + ZPE = -229.677132

Enthalpy (298K) = -229.671541

Free Energy (298K) = -229.704913

AcO^-

Number of imaginary freguencies: 0

Charge = -1, Multiplicity = 1

C	1.344585000	-0.045939000	-0.000027000
H	1.725618000	-1.067900000	-0.002031000
H	1.728008000	0.481522000	-0.877844000
C	-0.187298000	-0.000559000	-0.000050000
O	-0.805181000	-1.095963000	0.000009000
O	-0.710442000	1.144412000	0.000007000
H	1.727631000	0.477774000	0.880214000

Energy (0K) = -229.2691625

Energy (0K) + ZPE = -229.220912

Enthalpy (298K) = -229.216422

Free Energy (298K) = -229.246774

1

Number of imaginary freguencies: 0

Charge = 0, Multiplicity = 1

Ni	0.000004000	-0.403429000	0.000004000
S	-1.596857000	-1.885977000	0.193416000
S	1.596849000	-1.885985000	-0.193448000
N	-1.355349000	0.998970000	-0.194183000
N	1.355352000	0.998976000	0.194172000
C	-3.026946000	-0.730969000	0.310430000

H	-3.590105000	-0.740301000	-0.625031000
H	-3.699854000	-1.074843000	1.097896000
C	-2.533684000	0.660903000	0.642368000
H	-3.321237000	1.413210000	0.495386000
H	-2.207237000	0.700700000	1.683675000
C	-1.748634000	1.089546000	-1.617741000
H	-2.120223000	0.126259000	-1.959573000
H	-0.886578000	1.354229000	-2.227741000
H	-2.525228000	1.853293000	-1.743850000
C	-0.720729000	2.270764000	0.233118000
H	-0.775696000	2.321865000	1.321476000
H	-1.263812000	3.134955000	-0.165026000
C	0.720738000	2.270743000	-0.233214000
H	0.775699000	2.321760000	-1.321577000
H	1.263828000	3.134960000	0.164863000
C	1.748582000	1.089619000	1.617740000
H	0.886507000	1.354332000	2.227699000
H	2.525174000	1.853369000	1.743844000
H	2.120160000	0.126348000	1.959632000
C	2.533725000	0.660882000	-0.642316000
H	3.321277000	1.413186000	-0.495309000
H	2.207329000	0.700661000	-1.683640000
C	3.026955000	-0.730989000	-0.310332000
H	3.590033000	-0.740321000	0.625177000
H	3.699932000	-1.074867000	-1.097738000

Energy (0K) = -2732.828359

Energy (0K) + ZPE = -2732.56024

Enthalpy (298K) = -2732.545229

Free Energy (298K) = -2732.599804

2e

Number of imaginary freguencies: 0

Charge = -1, Multiplicity = 2

Ni	0.000000000	0.568918000	0.000000000
S	1.844709000	1.918876000	0.390456000
S	-1.844709000	1.918876000	-0.390456000
N	1.405056000	-1.054408000	-0.281799000
N	-1.405057000	-1.054408000	0.281799000
C	3.153454000	0.635926000	0.242542000
H	3.612274000	0.688719000	-0.748958000
H	3.948625000	0.831592000	0.966698000
C	2.610707000	-0.759528000	0.505642000
H	3.392662000	-1.512343000	0.303491000
H	2.334635000	-0.838060000	1.560585000

C	1.735463000	-1.170977000	-1.704526000
H	2.139843000	-0.228251000	-2.072006000
H	0.838568000	-1.393174000	-2.282605000
H	2.474064000	-1.969670000	-1.878365000
C	0.734422000	-2.269921000	0.196322000
H	0.828502000	-2.299043000	1.284207000
H	1.220128000	-3.178789000	-0.190362000
C	-0.734423000	-2.269921000	-0.196323000
H	-0.828503000	-2.299042000	-1.284208000
H	-1.220129000	-3.178788000	0.190361000
C	-1.735463000	-1.170977000	1.704526000
H	-0.838568000	-1.393175000	2.282605000
H	-2.474063000	-1.969670000	1.878365000
H	-2.139843000	-0.228251000	2.072006000
C	-2.610708000	-0.759527000	-0.505642000
H	-3.392662000	-1.512343000	-0.303490000
H	-2.334636000	-0.838059000	-1.560585000
C	-3.153454000	0.635926000	-0.242541000
H	-3.612272000	0.688720000	0.748960000
H	-3.948626000	0.831593000	-0.966696000

Energy (0K) = -2732.95029

Energy (0K) + ZPE = -2732.686251

Enthalpy (298K) = -2732.669933

Free Energy (298K) = -2732.728806

2H

Number of imaginary freguencies: 0

Charge = 1, Multiplicity = 1

Ni	-0.032937000	-0.415471000	-0.075036000
S	-1.629458000	-1.886984000	0.040744000
S	1.560398000	-1.915363000	-0.392914000
N	-1.355828000	0.986512000	-0.204583000
N	1.354050000	0.958736000	0.163795000
C	-3.047664000	-0.733238000	0.255379000
H	-3.632736000	-0.697057000	-0.664896000
H	-3.696463000	-1.117005000	1.043736000
C	-2.528258000	0.632172000	0.641337000
H	-3.299366000	1.406323000	0.537481000
H	-2.182339000	0.622494000	1.676650000
C	-1.768881000	1.131819000	-1.621705000
H	-2.157483000	0.186209000	-1.991078000
H	-0.912497000	1.409136000	-2.233569000
H	-2.536428000	1.908991000	-1.701874000
C	-0.707977000	2.243848000	0.259590000

H	-0.755890000	2.261737000	1.348928000
H	-1.252758000	3.118296000	-0.109127000
C	0.726757000	2.251587000	-0.220972000
H	0.773939000	2.336274000	-1.307086000
H	1.281212000	3.095456000	0.201268000
C	1.758158000	1.001479000	1.588836000
H	0.902685000	1.255532000	2.211541000
H	2.542552000	1.752565000	1.730194000
H	2.127349000	0.030129000	1.910919000
C	2.516091000	0.637648000	-0.698552000
H	3.328778000	1.353751000	-0.528440000
H	2.189758000	0.734963000	-1.735164000
C	3.013029000	-0.770366000	-0.439731000
H	3.551350000	-0.867944000	0.500392000
H	3.666026000	-1.100623000	-1.245623000
H	1.755084000	-2.424675000	0.841230000

Energy (0K) = -2733.262996

Energy (0K) + ZPE = -2732.984698

Enthalpy (298K) = -2732.969299

Free Energy (298K) = -2733.024848

3

Number of imaginary freguencies: 0

Charge = 0, Multiplicity = 2

Ni	-0.044652000	-0.603702000	-0.035698000
S	-1.803995000	-1.974104000	0.453484000
S	1.714858000	-1.932475000	-0.701589000
N	-1.424285000	1.004053000	-0.241721000
N	1.398681000	0.952320000	0.209697000
C	-3.130259000	-0.702316000	0.366639000
H	-3.632617000	-0.763894000	-0.602564000
H	-3.886649000	-0.909088000	1.127649000
C	-2.589921000	0.698021000	0.605012000
H	-3.385284000	1.444031000	0.440977000
H	-2.263279000	0.777866000	1.645043000
C	-1.826217000	1.138268000	-1.646376000
H	-2.249077000	0.199673000	-2.003283000
H	-0.959357000	1.368091000	-2.265839000
H	-2.571684000	1.938059000	-1.770641000
C	-0.721875000	2.211435000	0.217046000
H	-0.778610000	2.240766000	1.307155000
H	-1.206597000	3.126460000	-0.152054000
C	0.730912000	2.191282000	-0.229441000
H	0.785892000	2.232170000	-1.319309000

H	1.250307000	3.081093000	0.152844000
C	1.771413000	1.041022000	1.628459000
H	0.893093000	1.267146000	2.231777000
H	2.525732000	1.824562000	1.791145000
H	2.169636000	0.087886000	1.975586000
C	2.579890000	0.667041000	-0.618057000
H	3.395325000	1.372467000	-0.398584000
H	2.294490000	0.809980000	-1.662974000
C	3.098910000	-0.747723000	-0.430009000
H	3.498562000	-0.912156000	0.569303000
H	3.888695000	-0.949691000	-1.152893000
H	2.028216000	-2.791611000	0.290888000

Energy (0K) = -2733.413467

Energy (0K) + ZPE = -2733.139297

Enthalpy (298K) = -2733.122651

Free Energy (298K) = -2733.18204

4e

Number of imaginary freguencies: 0

Charge = -1, Multiplicity = 3

Ni	-0.053392000	-0.635182000	-0.081153000
S	-1.876978000	-1.989849000	0.319374000
S	1.748643000	-2.001089000	-0.540531000
N	-1.434847000	1.005187000	-0.241971000
N	1.394750000	0.942400000	0.179224000
C	-3.178478000	-0.692018000	0.280112000
H	-3.676833000	-0.699129000	-0.693444000
H	-3.945055000	-0.913526000	1.027070000
C	-2.610876000	0.685552000	0.581711000
H	-3.391229000	1.454089000	0.445450000
H	-2.290750000	0.714481000	1.626607000
C	-1.823773000	1.193601000	-1.642425000
H	-2.249559000	0.271149000	-2.036293000
H	-0.950385000	1.438419000	-2.246767000
H	-2.563031000	2.003288000	-1.745264000
C	-0.726778000	2.187650000	0.266488000
H	-0.769045000	2.159149000	1.357718000
H	-1.218850000	3.120143000	-0.048194000
C	0.722178000	2.193540000	-0.194727000
H	0.766771000	2.286429000	-1.282170000
H	1.239326000	3.070576000	0.221677000
C	1.816354000	0.969790000	1.582684000
H	0.967134000	1.204676000	2.224751000
H	2.603153000	1.722240000	1.747875000

H	2.193584000	-0.011860000	1.874688000
C	2.538648000	0.661953000	-0.698314000
H	3.348616000	1.390234000	-0.521960000
H	2.196064000	0.788079000	-1.728294000
C	3.080444000	-0.748235000	-0.519549000
H	3.621033000	-0.852333000	0.427746000
H	3.789635000	-0.954033000	-1.323779000
H	2.283777000	-2.578441000	1.163332000

Energy (0K) = -2733.487116

Energy (0K) + ZPE =-2733.219577

Enthalpy (298K) = -2733.202534

Free Energy (298K) = -2733.262684

4H

Number of imaginary freguencies: 0

Charge = 1, Multiplicity = 2

Ni	0.001258000	-0.482926000	-0.014262000
S	-1.802012000	-1.901095000	0.400871000
S	1.787215000	-1.839662000	-0.548920000
N	-1.397449000	1.067535000	-0.308286000
N	1.394541000	1.061657000	0.323544000
C	-3.125450000	-0.650014000	0.182023000
H	-3.475356000	-0.786230000	-0.841542000
H	-3.953063000	-0.893307000	0.847324000
C	-2.625877000	0.759703000	0.442514000
H	-3.425134000	1.472836000	0.193032000
H	-2.402894000	0.869108000	1.505893000
C	-1.691071000	1.214798000	-1.743572000
H	-2.083517000	0.283067000	-2.149458000
H	-0.778427000	1.450848000	-2.289009000
H	-2.423923000	2.015168000	-1.913681000
C	-0.741762000	2.284420000	0.210578000
H	-0.864381000	2.295716000	1.295230000
H	-1.222819000	3.191910000	-0.177133000
C	0.735024000	2.294894000	-0.148268000
H	0.857694000	2.348184000	-1.231716000
H	1.212191000	3.188890000	0.274050000
C	1.691866000	1.151773000	1.761846000
H	0.781940000	1.373102000	2.318057000
H	2.430866000	1.939681000	1.961130000
H	2.077586000	0.201605000	2.129834000
C	2.618517000	0.780177000	-0.443343000
H	3.416080000	1.492345000	-0.187226000
H	2.384413000	0.913788000	-1.501840000

C	3.137337000	-0.629104000	-0.217132000
H	3.489157000	-0.784706000	0.800966000
H	3.961528000	-0.832572000	-0.899537000
H	2.001304000	-2.647164000	0.509239000
H	-1.752886000	-1.862462000	1.749840000

Energy (0K) = -2733.867767
Energy (0K) + ZPE =-2733.583631
Enthalpy (298K) = -2733.566594
Free Energy (298K) = -2733.626588

5

Number of imaginary freguencies: 0
Charge = 0, Multiplicity = 1

Ni	0.201326000	-0.365133000	-0.428055000
S	1.703415000	-1.875383000	-0.731484000
S	-2.711689000	-1.785339000	0.867141000
N	1.499471000	0.780272000	0.558492000
N	-1.107180000	1.154849000	-0.362917000
C	3.124380000	-1.006394000	0.061147000
H	3.279995000	-1.388545000	1.072753000
H	4.032942000	-1.216181000	-0.507034000
C	2.864549000	0.484395000	0.059817000
H	3.607528000	1.023201000	0.665503000
H	2.921105000	0.857910000	-0.964739000
C	1.434079000	0.549267000	2.013358000
H	1.713736000	-0.479806000	2.230834000
H	0.420161000	0.702201000	2.378190000
H	2.112819000	1.230008000	2.542225000
C	1.079565000	2.154735000	0.216733000
H	1.377417000	2.343925000	-0.816494000
H	1.580150000	2.899148000	0.849200000
C	-0.421782000	2.261834000	0.370320000
H	-0.695589000	2.186523000	1.422804000
H	-0.779691000	3.235265000	0.016660000
C	-1.289264000	1.562029000	-1.775245000
H	-0.319448000	1.751625000	-2.234900000
H	-1.898312000	2.473211000	-1.830692000
H	-1.774174000	0.763299000	-2.331948000
C	-2.443821000	0.955526000	0.263239000
H	-3.067343000	1.821491000	-0.001380000
H	-2.309578000	0.968521000	1.345592000
C	-3.180111000	-0.318089000	-0.115117000
H	-3.082464000	-0.553191000	-1.175335000
H	-4.242390000	-0.172873000	0.088121000

H	-1.446245000	-1.838639000	0.356169000
H	-0.686974000	-1.217480000	-1.225019000

Energy (0K) = -2734.017655
Energy (0K) + ZPE =-2733.734666
Enthalpy (298K) = -2733.718116
Free Energy (298K) = -2733.777144

TS

Number of imaginary freguencies: 1
Charge = 0, Multiplicity = 1

Ni	0.108718000	-0.362908000	-0.397525000
S	1.859353000	-1.651675000	-0.723090000
S	-1.718617000	-1.954972000	0.901728000
N	1.257679000	0.915631000	0.489192000
N	-1.367963000	1.021399000	-0.333153000
C	3.154075000	-0.574581000	-0.003148000
H	3.399632000	-0.898076000	1.009794000
H	4.060683000	-0.658934000	-0.604732000
C	2.652402000	0.845060000	-0.036464000
H	3.286774000	1.525340000	0.546916000
H	2.620742000	1.199057000	-1.068175000
C	1.256063000	0.659215000	1.948031000
H	1.673606000	-0.325672000	2.144216000
H	0.238212000	0.670347000	2.331653000
H	1.852085000	1.422672000	2.459366000
C	0.680464000	2.251366000	0.187389000
H	0.920430000	2.484578000	-0.851172000
H	1.139965000	3.019273000	0.819690000
C	-0.809733000	2.193468000	0.397709000
H	-1.037584000	2.072248000	1.455888000
H	-1.289518000	3.120658000	0.068229000
C	-1.644118000	1.408865000	-1.736410000
H	-0.716886000	1.679656000	-2.241253000
H	-2.332600000	2.260884000	-1.762716000
H	-2.094102000	0.572232000	-2.268043000
C	-2.641599000	0.587413000	0.320236000
H	-3.449057000	1.236051000	-0.045833000
H	-2.535229000	0.755600000	1.392505000
C	-2.965841000	-0.874197000	0.106582000
H	-3.046694000	-1.099356000	-0.963270000
H	-3.953224000	-1.062647000	0.535335000
H	-0.830272000	-1.528676000	-1.121618000
H	-0.521115000	-1.116323000	-1.760113000

Energy (0K) = -2733.994216

Energy (0K) + ZPE =-2733.710911
Enthalpy (298K) = -2733.695169
Free Energy (298K) =-2733.752078

H_2
Number of imaginary freguencies: 0
Charge = 0, Multiplicity = 1

H	0.000000000	0.000000000	0.372859000
H	0.000000000	0.000000000	-0.372859000

Energy (0K) = -1.2153039
Energy (0K) + ZPE = -1.205254
Enthalpy (298K) = -1.201949
Free Energy (298K) = -1.216748