Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Proton Reduction by a Nickel Complex with Internal Quinoline Moiety for Proton-Relay

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Supporting Information

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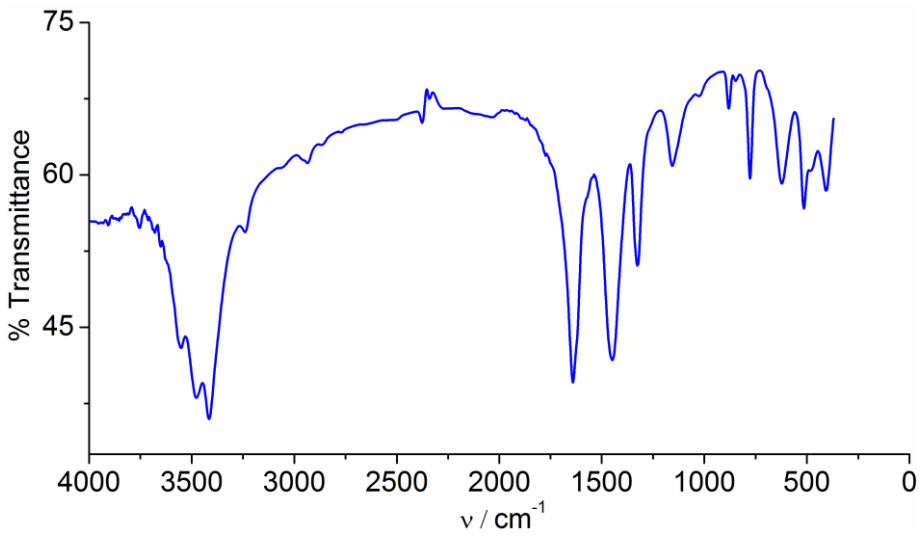

Figure S1. IR Spectra of the Ligand $DQPDH_2$.

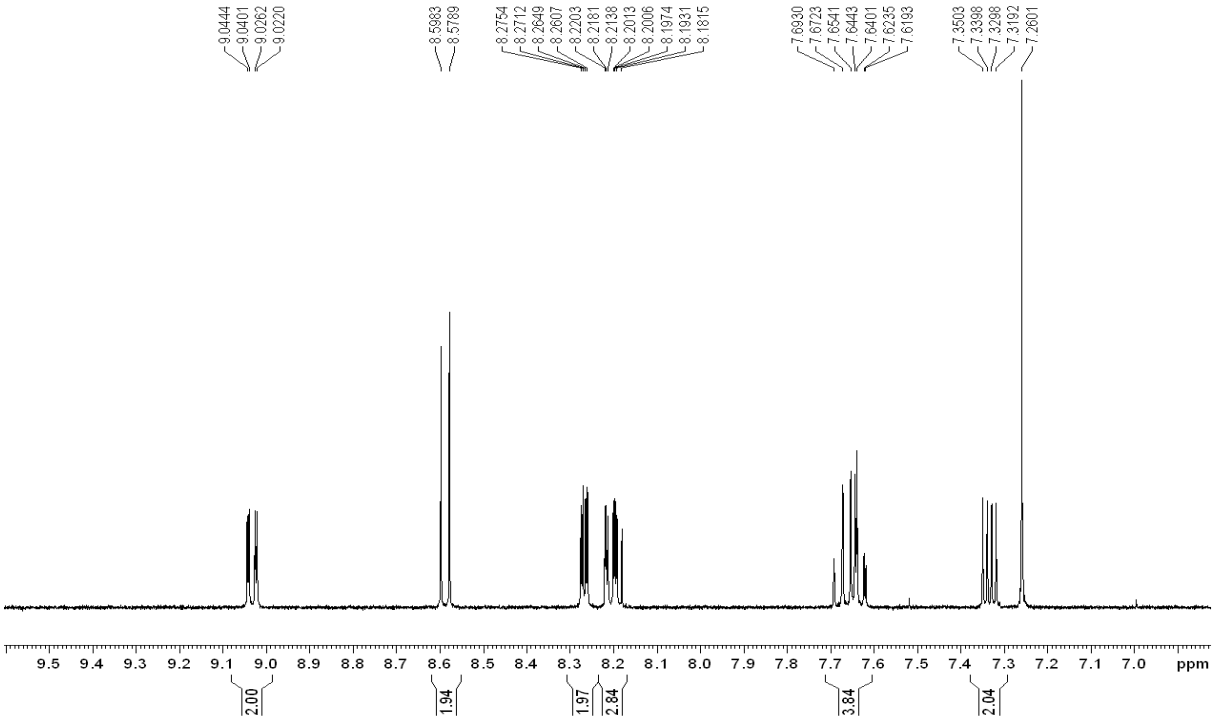

Figure S2. ^1H NMR of **$DQPDH_2$** in $CDCl_3$.

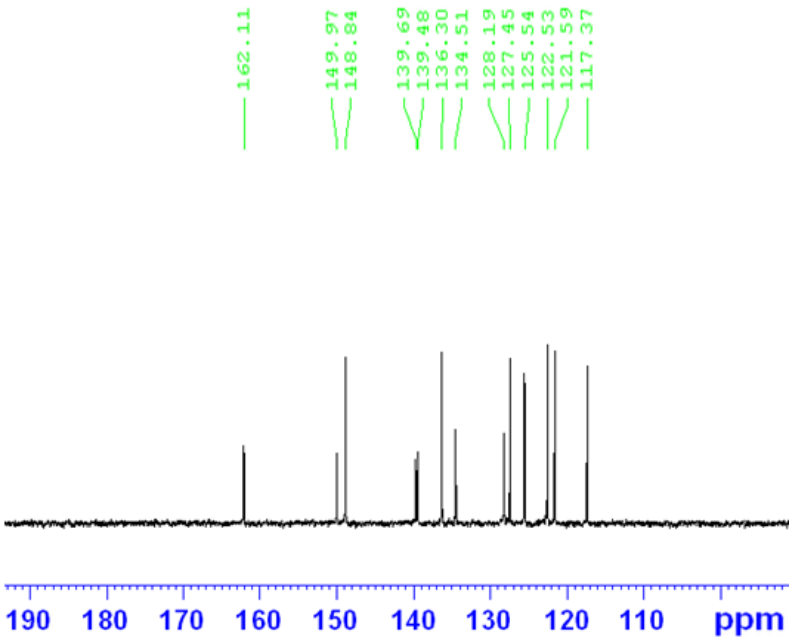

Figure S3. ^{13}C NMR of $DQPDH_2$ in $CDCl_3$.

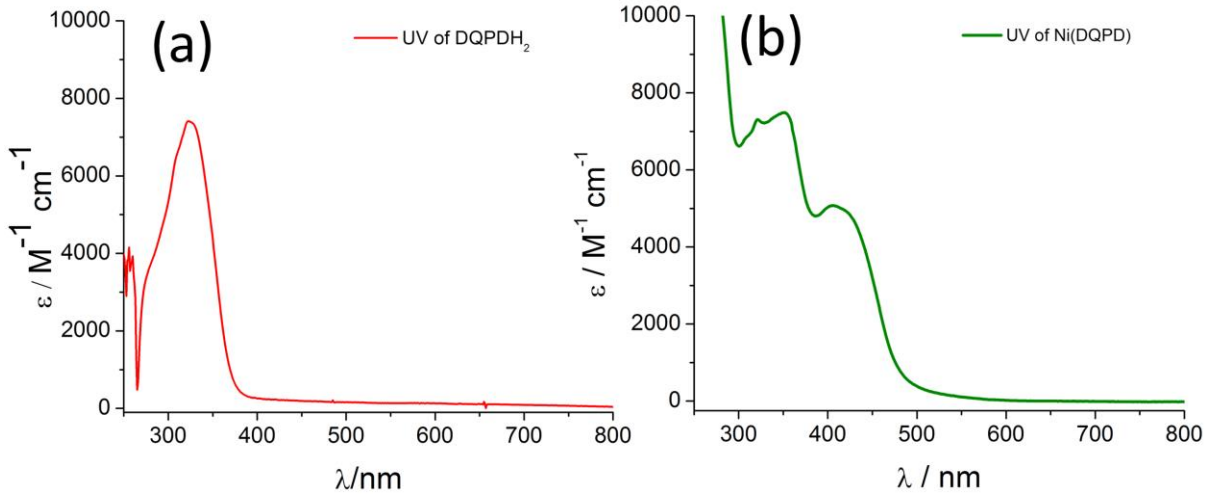

Figure S4. The UV-Visible spectrum of 0.1 mM (a) **$DQPDH_2$** ligand and (b) **Ni(DQPD)** complex in DMF/H_2O (95:5, v/v).

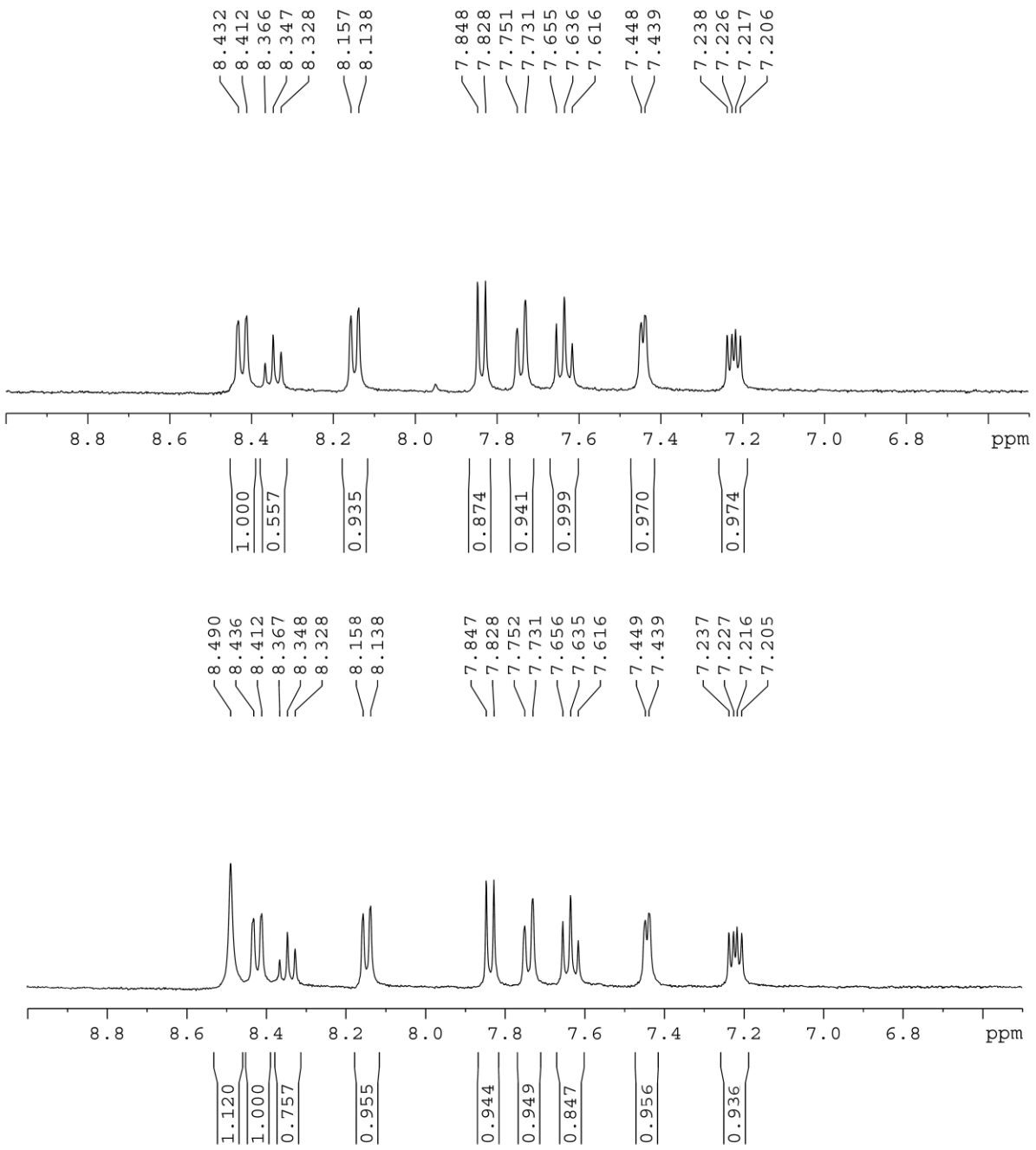

Figure S5. ^{1}H NMR of **Ni(DQPD)** (top) and **Ni(DQPDH)** (bottom) complex in DMSO-D_6.

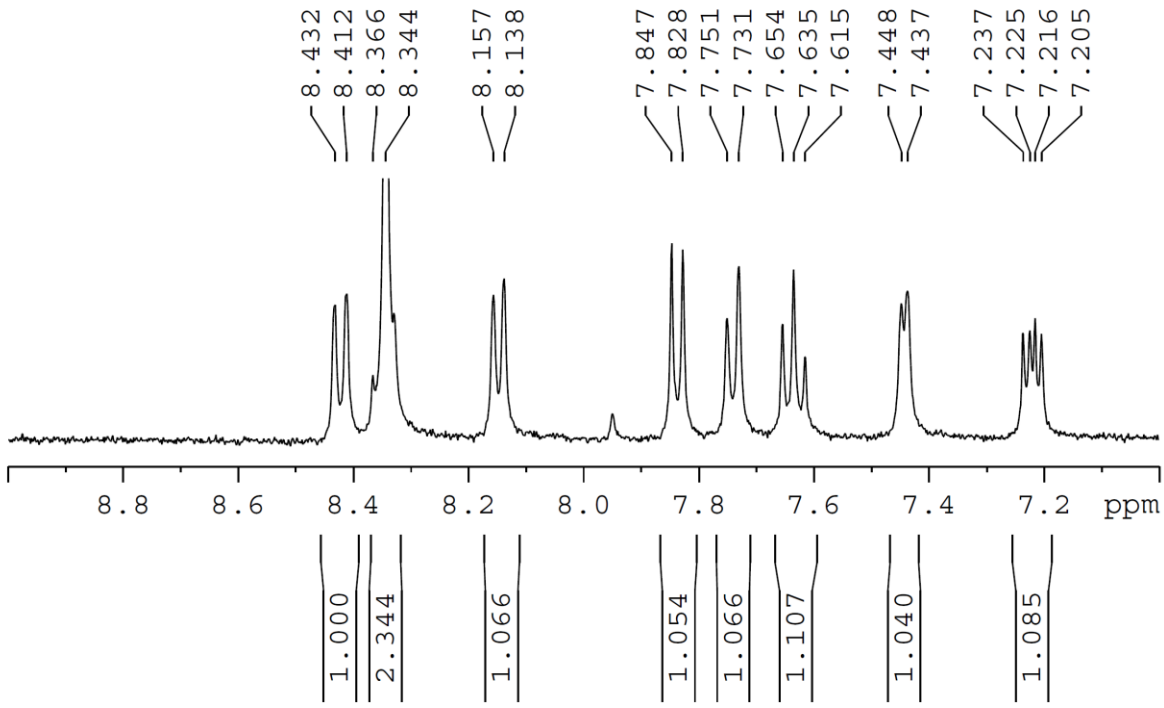

Figure S6. ^{1}H NMR of **Ni(DQPD)** complex in DMSO-D_6 in presence of acetic acid.

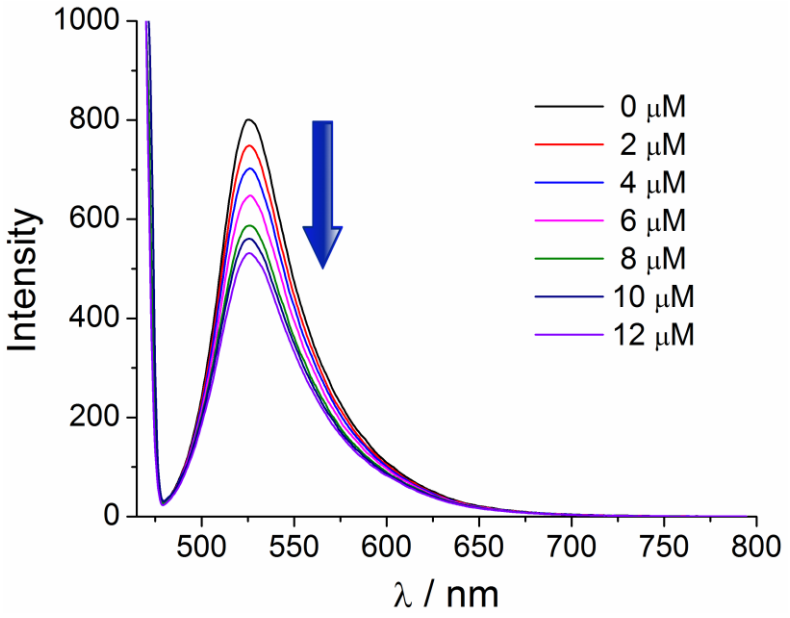

Figure S7. The fluorescence quenching of fluorescein by **Ni(DQPD)** complex in 70:30 DMF/H_2O.

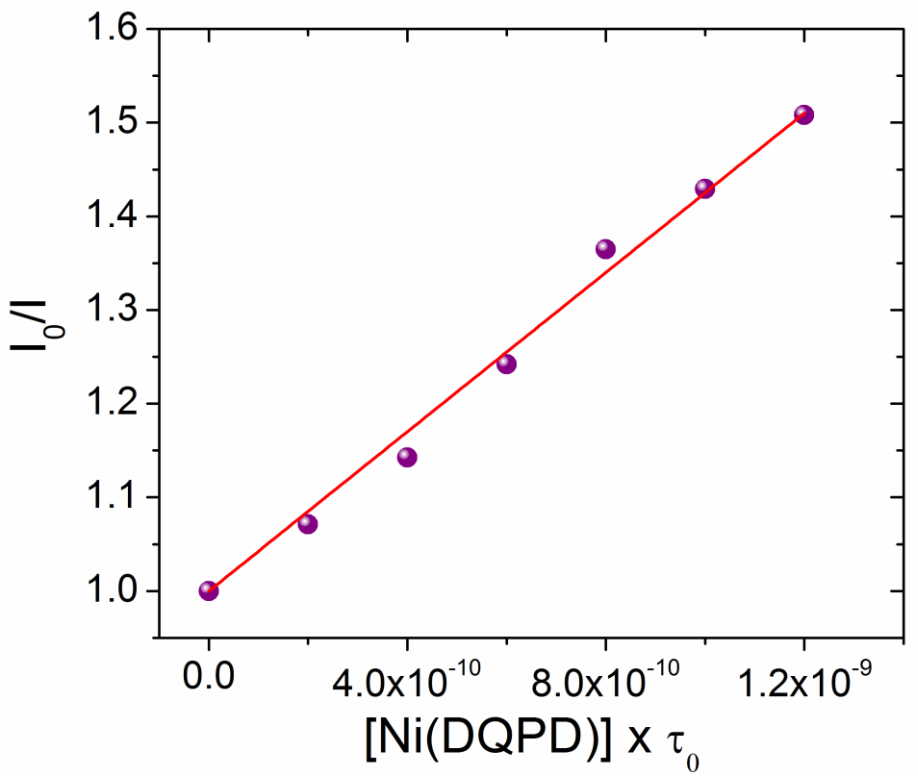

Figure S8. Stern-Volmer plot of the emission quenching of fluorescein solution 5×10^{-8} M concentration in 70:30 DMF/H_2O by **Ni(DQPD)**.

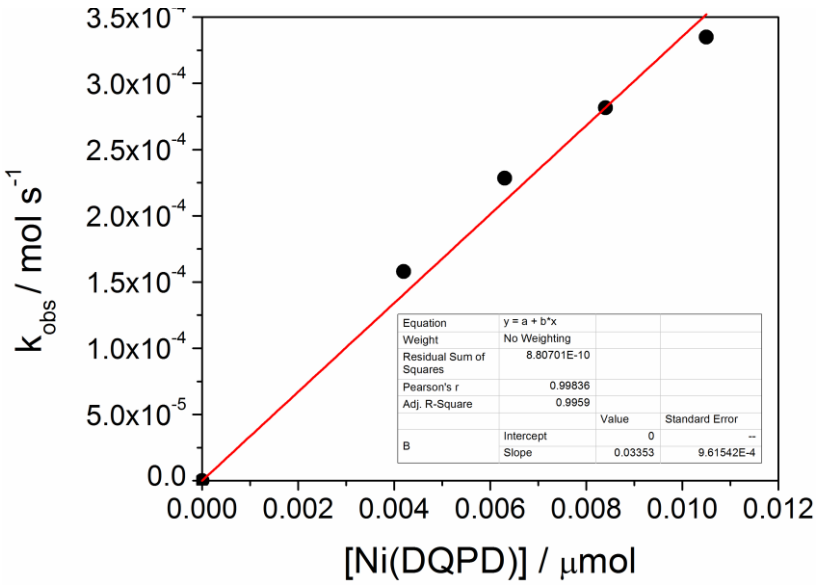

Figure S9. Rate of Hydrogen production with varied concentration of **Ni(DQPD)** complex with the presence of 2mM fluorescein in 2 mL of 70:30 DMF/H_2O.

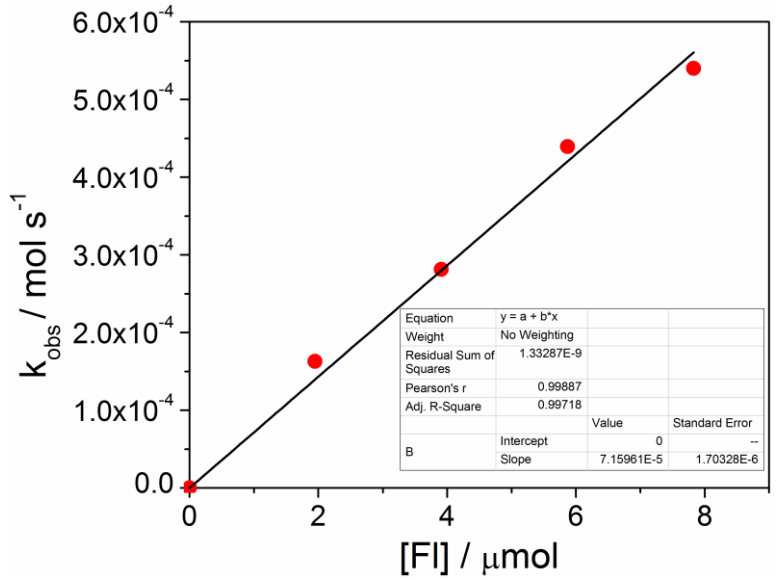

Figure S10. Rate of Hydrogen production by **Ni(DQPD)** complex with varied concentration of fluorescein in 70:30 DMF/H_2O.

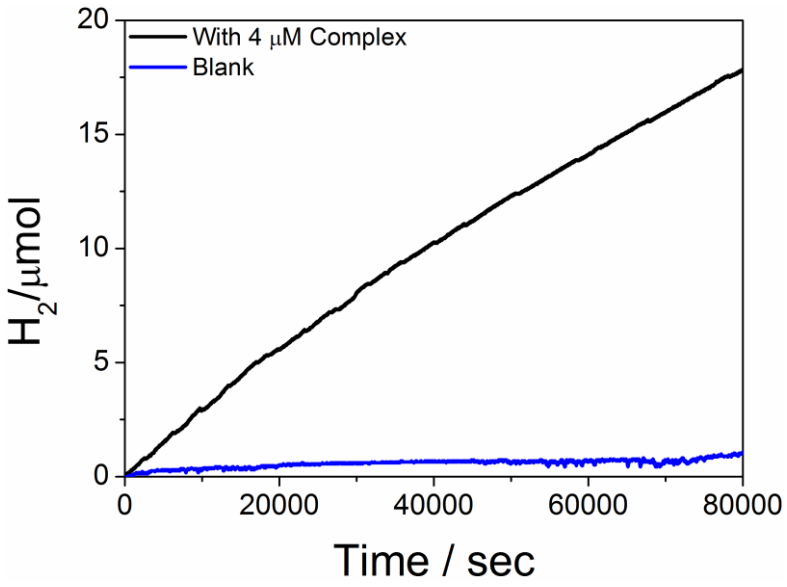

Figure S11. Hydrogen evolution by 4 x 10^{-6} M **Ni(DQPD)** complex in presence of 2 mM fluorescein in 70:30 DMF/H_2O (black) and blank solution without catalyst (blue).

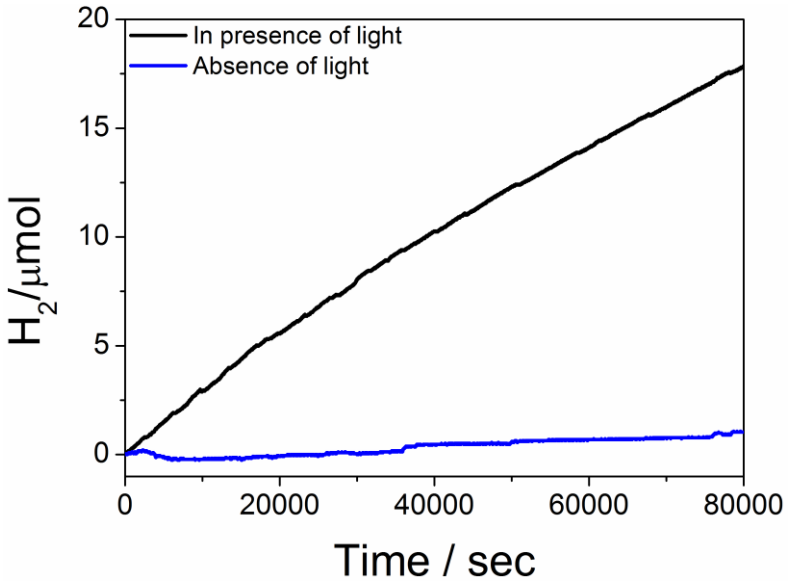

Figure S12. Hydrogen evolution by 4 x 10^{-6} M **Ni(DQPD)** complex in presence of 2 mM fluorescein in 70:30 DMF/H_2O in presence of light (black) and under dark condition (blue).

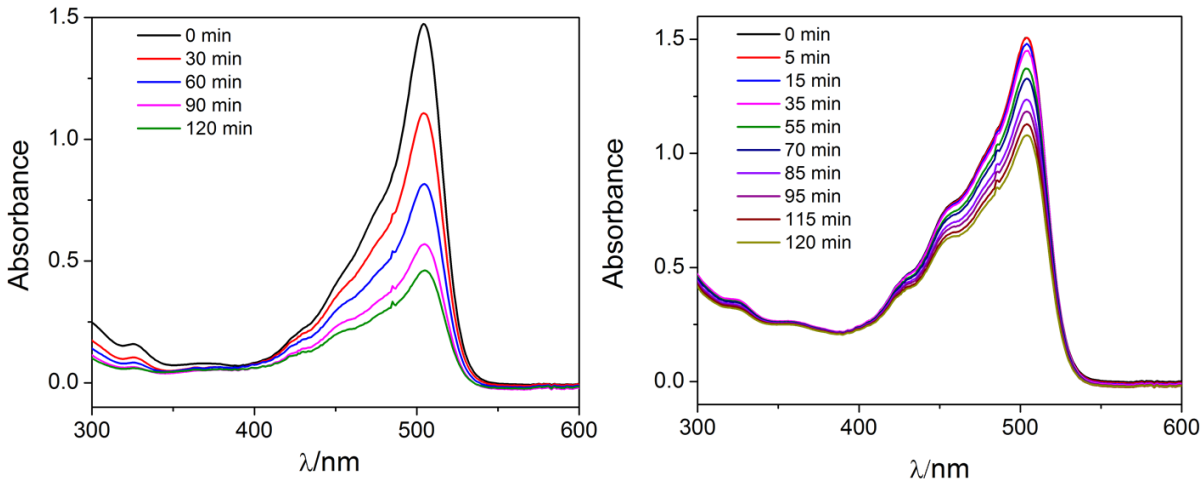

Figure S13. UV-vis absorption spectral change of the system containing fluorescein (4 x 10^{-5} M) and (4 x 10^{-5}) M TEA in 70:30 DMF/H_2O (left). UV-vis absorption spectral change of the system containing fluorescein (4 x 10^{-5} M), **Ni(DQPD)** (8 x 10^{-5} M), (4 x 10^{-5}) M TEA in 70:30 DMF/H_2O (left)

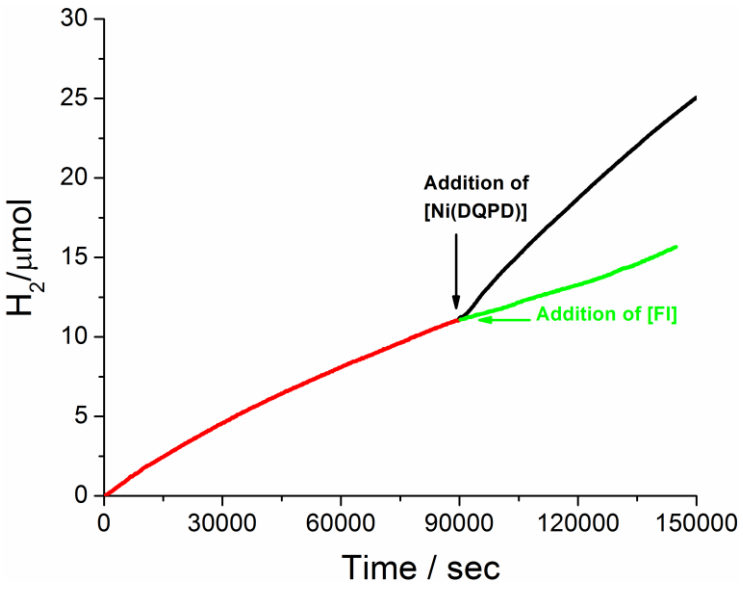

Figure S14. Hydrogen production with 4 x 10^{-6} M **Ni(DQPD)** complex in 70:30 DMF/H_2O in presence of 1 mM fluorescein (Top) and [TEA] = 0.36 M and the recovery of the photocatalytic activity by the addition of extra Fl (1.0 mM) or **Ni(DQPD)** 4 x 10^{-6} after 25 h irradiation.

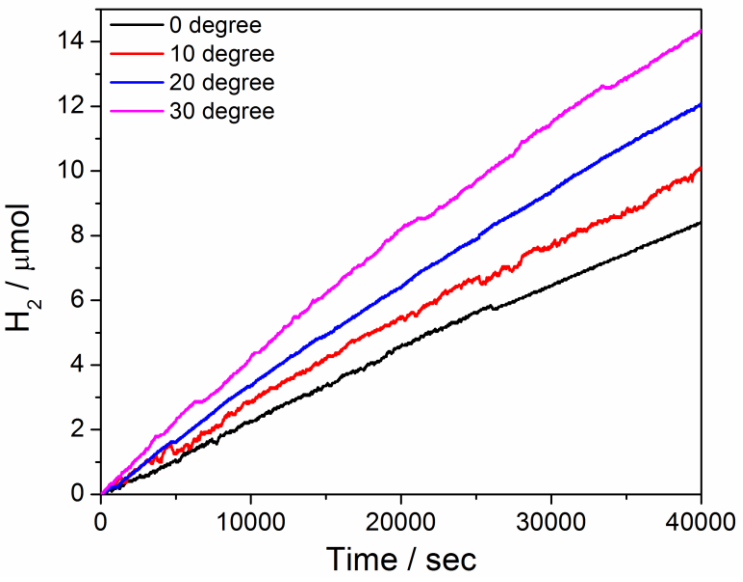

Figure S15. Rate of Hydrogen production at varied temperature by 5 x 10^{-6} M [**Ni(DQPD)**] complex in presence of 2 mM fluorescein in 70:30 DMF/H_2O.

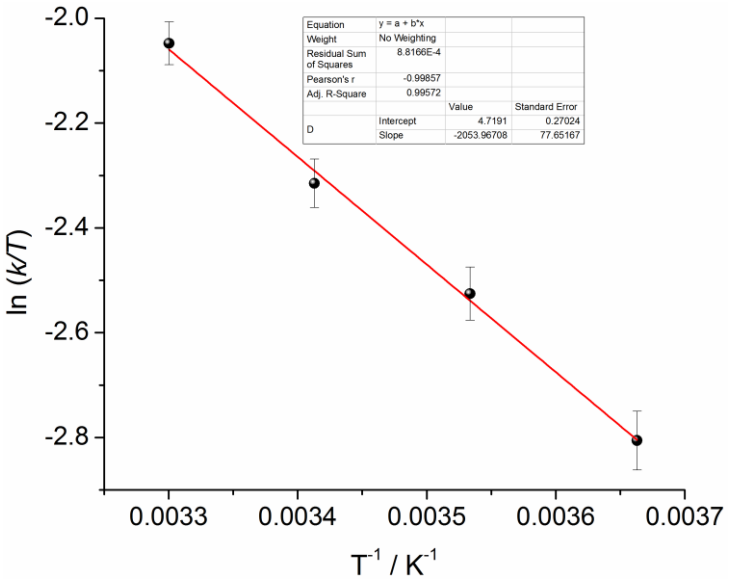

Figure S16. Eyring-Polanyi plot of Hydrogen evolution at varied temperature by 5 x 10^{-6} M [**Ni(DQPD)**] complex in presence of 2 mM fluorescein in 70:30 DMF/H_2O.

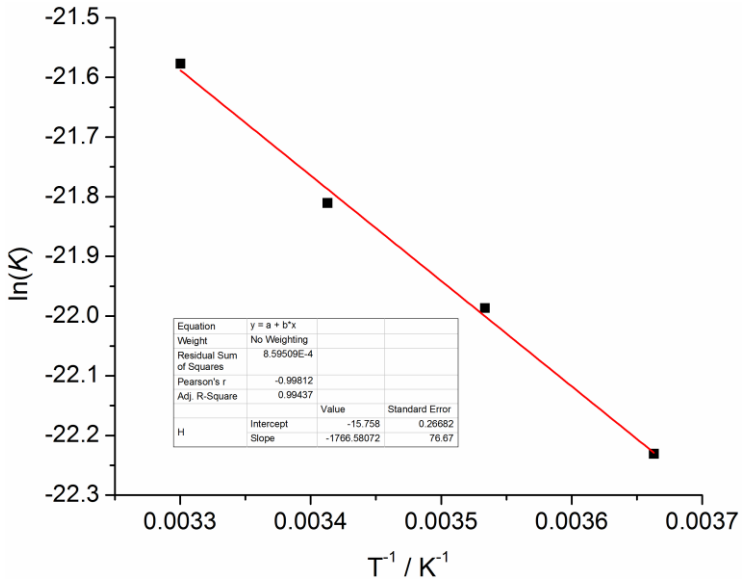

Figure S17. Arrhenius plot of Hydrogen evolution at varied temperature by 5 x 10^{-6} M [**Ni(DQPD)**] complex in presence of 2 mM fluorescein in 70:30 DMF/H_2O.

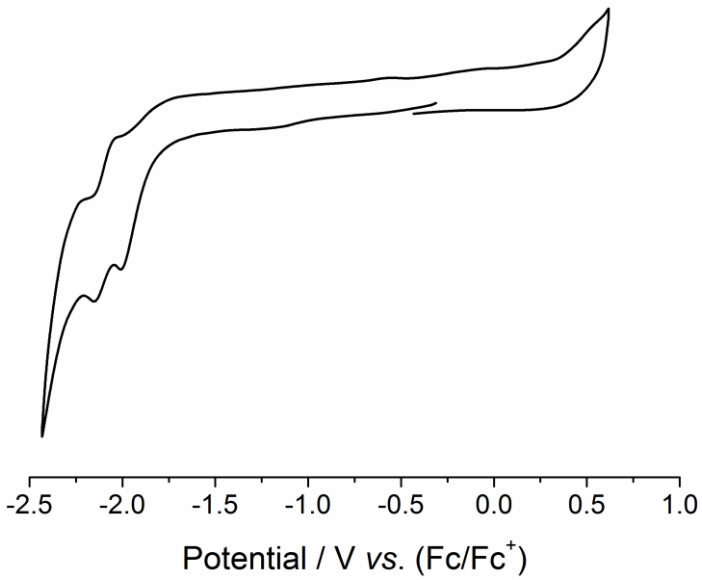

Figure S18. CV of 1.0 mM **DQPDH$_2$** in DMF, 0.1 M TBAP, and an electrochemical potential scan rate of 100 mV s^{-1}.

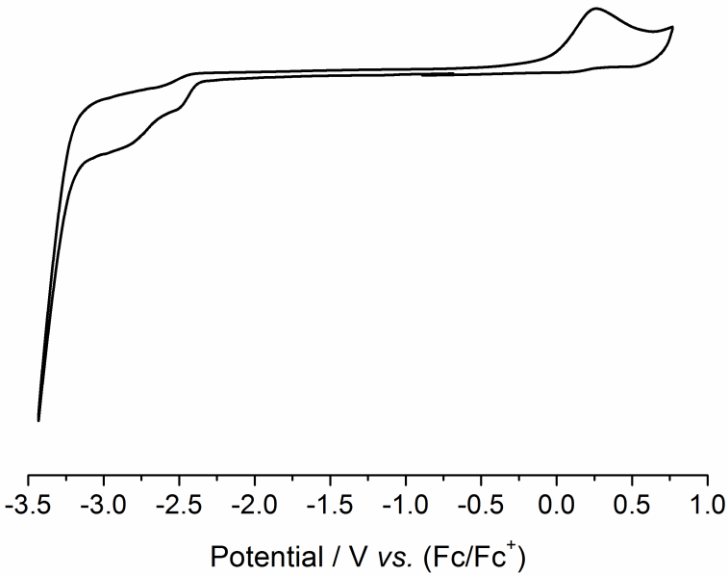

Figure S19. CV of 1.0 mM **DQPDH$_2$** in DMF, 0.1 M TBAP, and an electrochemical potential scan rate of 100 mV s^{-1} under N_2 after addition of 2 equivalents of NaH.

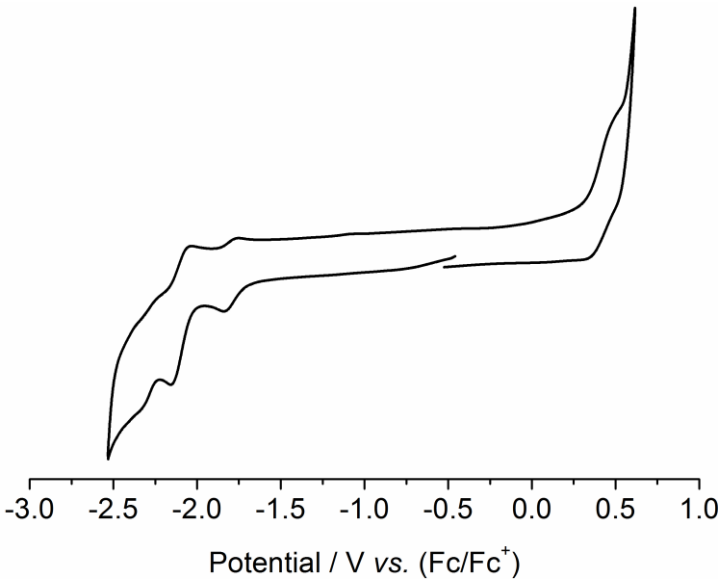

Figure S20. CV of **Ni(DQPD)** complex prepared *in situ* from, 1.0 mM **DQPDH2** in DMF, 0.1 M TBAP, and an electrochemical potential scan rate of 100 mV s^{-1} under N_2 after addition of 2 equivalents of NaH, following one equiv. of $NiCl_2 \cdot 6H_2O$.

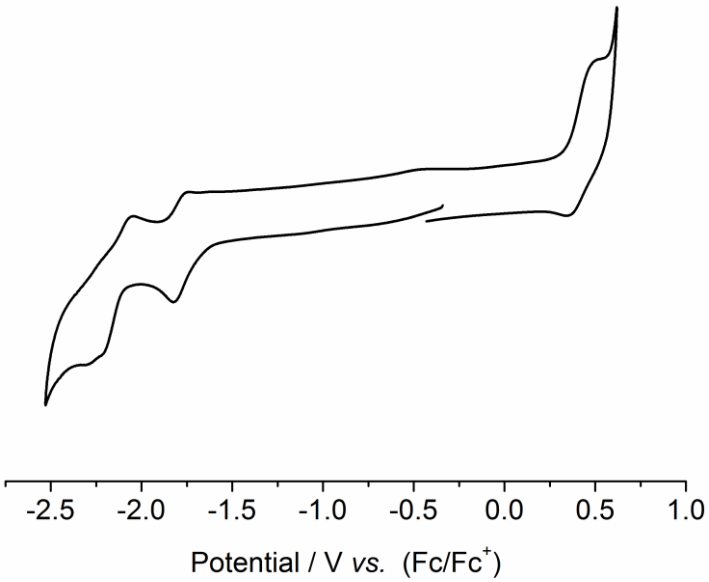

Figure S21. CV of 1.0 mM isolated **Ni(DQPD)** complex in DMF, 0.1 M TBAP, and an electrochemical potential scan rate of 100 mV s^{-1} under N_2.

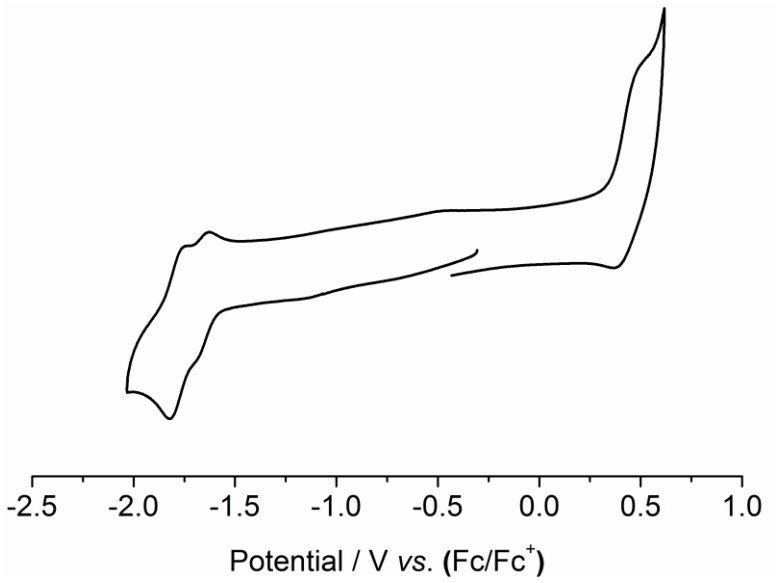

Figure S22. CV of 1.0 mM isolated **Ni(DQPD)** complex in presence one equiv. of AcOH, in DMF, 0.1 M TBAP, and an electrochemical potential scan rate of 100 mV s^{-1} under N_2.

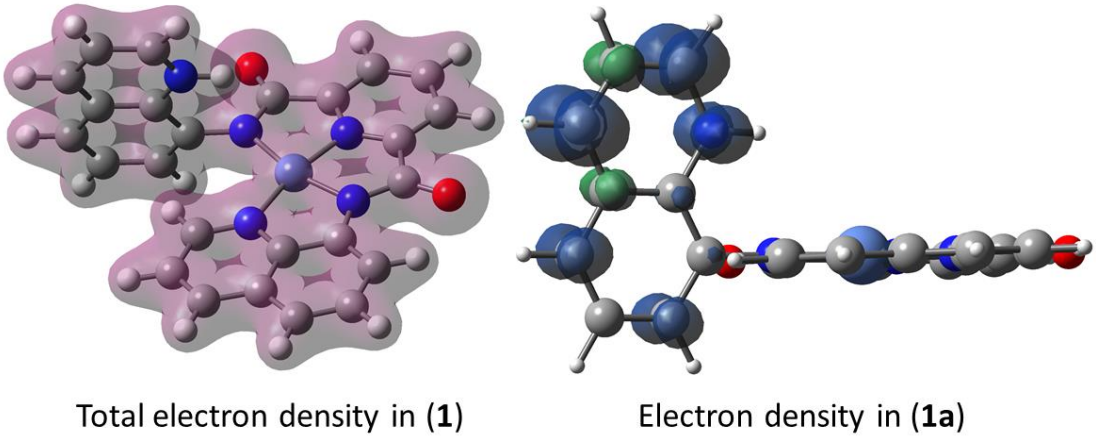

Figure S23. The electron density in (**1**) and (**1a**).

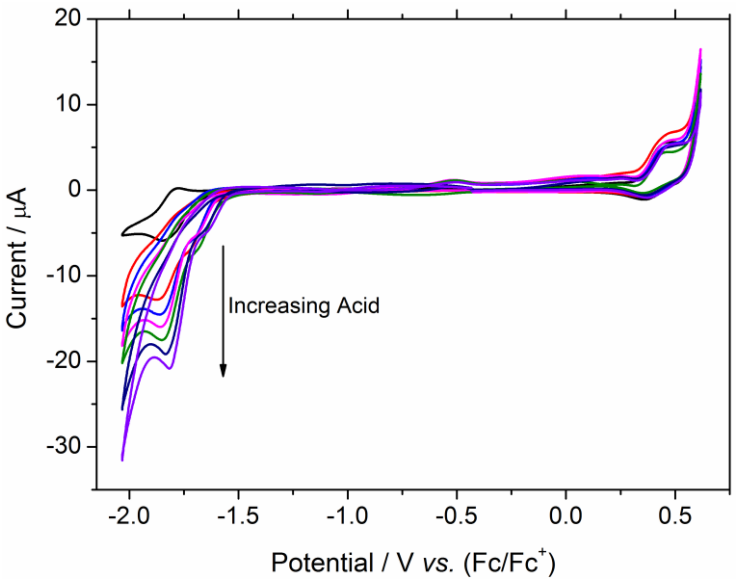

Figure S24. CV of **Ni(DQPD)** in the presence of varying concentrations of CH_3COOH. The experimental conditions are 0.5 mM **Ni(DQPD)** in DMF/H_2O (95:5, v/v), 0.1 M TBAP, and an electrochemical potential scan rate of 100 mV s^{-1}. The CH_3COOH equivalents are 2.5, 5.0, 7.5, 10.0, 12.5 and 15.0 respectively from red to violet color.

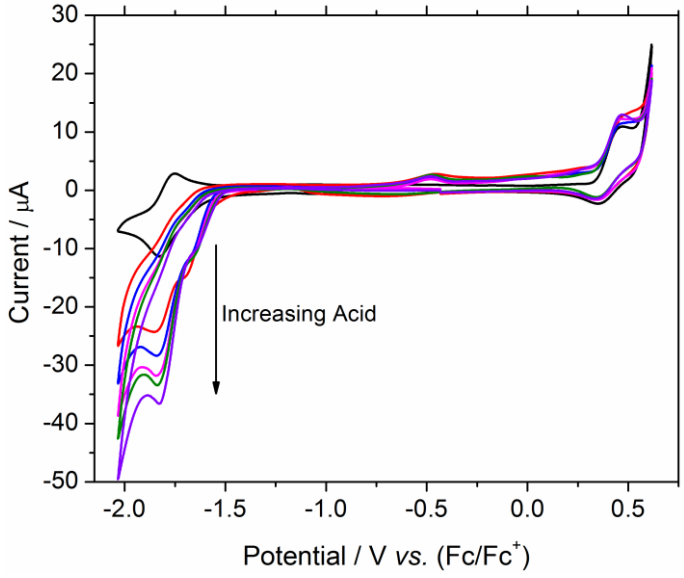

Figure S25. CV of **Ni(DQPD)** in the presence of varying concentrations of CH_3COOH. The experimental conditions are 1.0 mM **Ni(DQPD)** in DMF/H_2O (95:5, v/v), 0.1 M TBAP, and an electrochemical potential scan rate of 100 mV s^{-1}. The CH_3COOH equivalents are 2.5, 5.0, 7.5, 10.0, and 15.0 respectively from red to violet color.

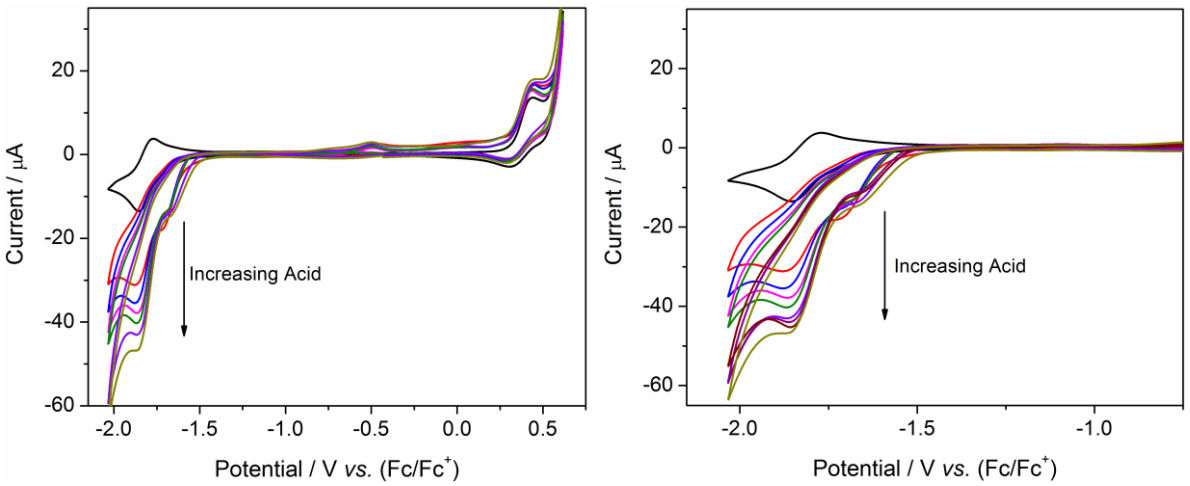

Figure S26. CV of **Ni(DQPD)** in the presence of varying concentrations of CH_3COOH. The experimental conditions are 1.5 mM **Ni(DQPD)** in DMF/H_2O (95:5, v/v), 0.1 M TBAP, and an electrochemical potential scan rate of 100 mV s^{-1}. The CH_3COOH equivalents are 2.5, 5.0, 7.5, 10.0, 15.0 and 22.5 respectively from red to brown color. (Right side 2.5, 5.0, 7.5, 10.0, 15.0, 17.5, 20 and 22.5).

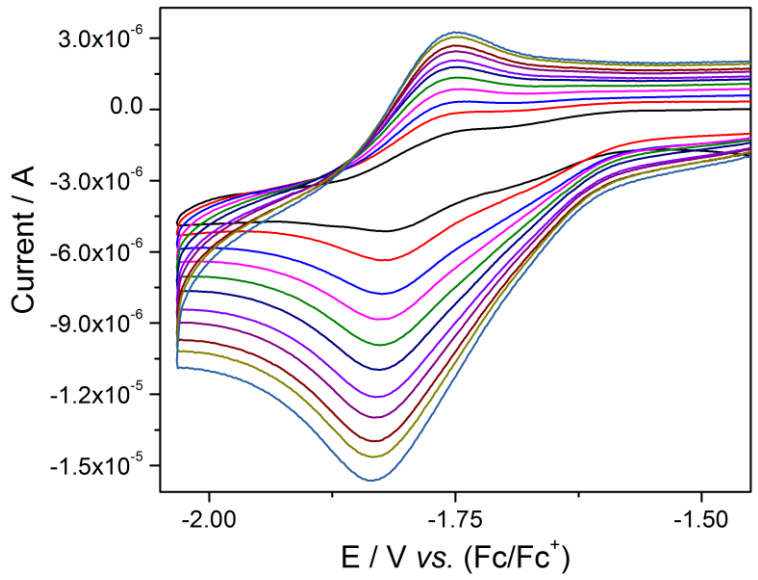

Figure S27. Cyclic voltammograms of 1.0 mM **Ni(DQPD)** complex and in presence of 0.1 M TBAP as supporting electrolyte in DMF/H_2O (95:5, v/v) solution at varying scan rates.

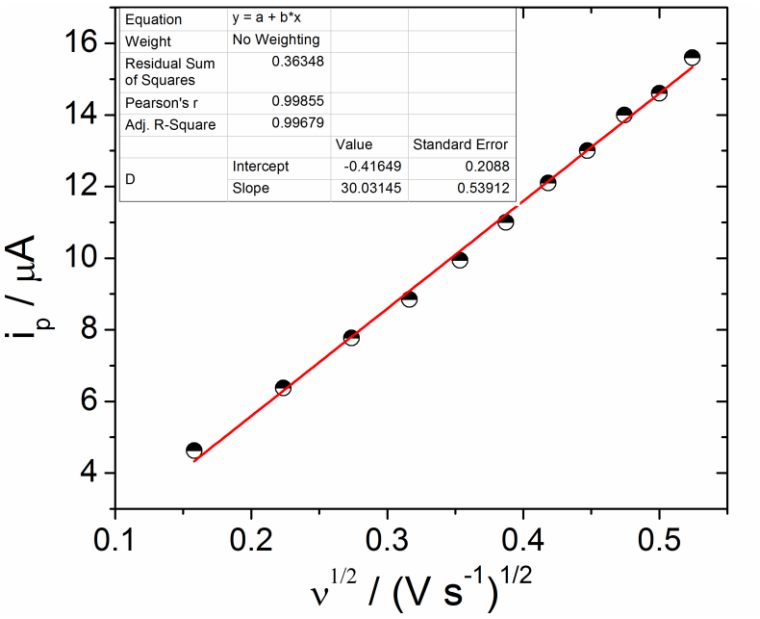

Figure S28. Peak current (i_p) *vs.* square root of scan rate scan rate ($\nu^{1/2}$) with linear fitted slope 3.0×10^{-5} A $V^{-1/2}$ $s^{1/2}$.

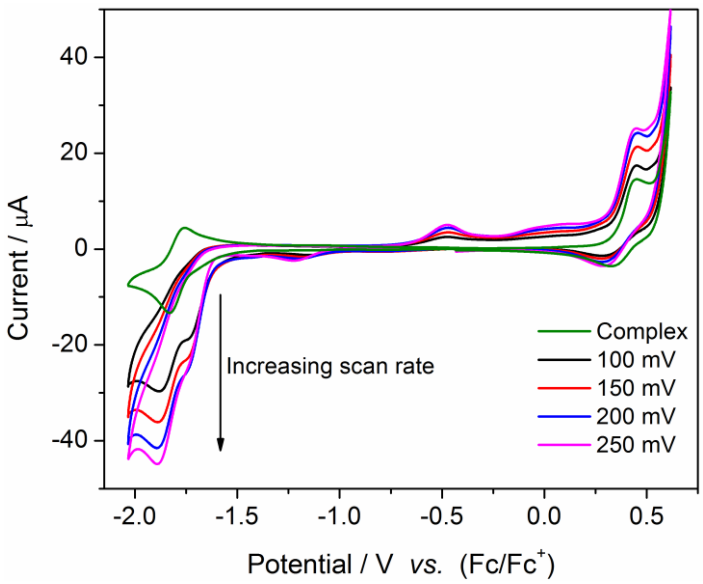

Figure S29. CV of 1.5 mM **Ni(DQPD)** in DMF/H_2O (95:5, v/v) 0.1 M TBAP and scan rate 100 mV/s (green). Catalytic current in presence 2.5equivalent of CH_3COOH at a varying scan rate, of 100, 150, 200, and 250 mV s^{-1} (black to pink color respectively).

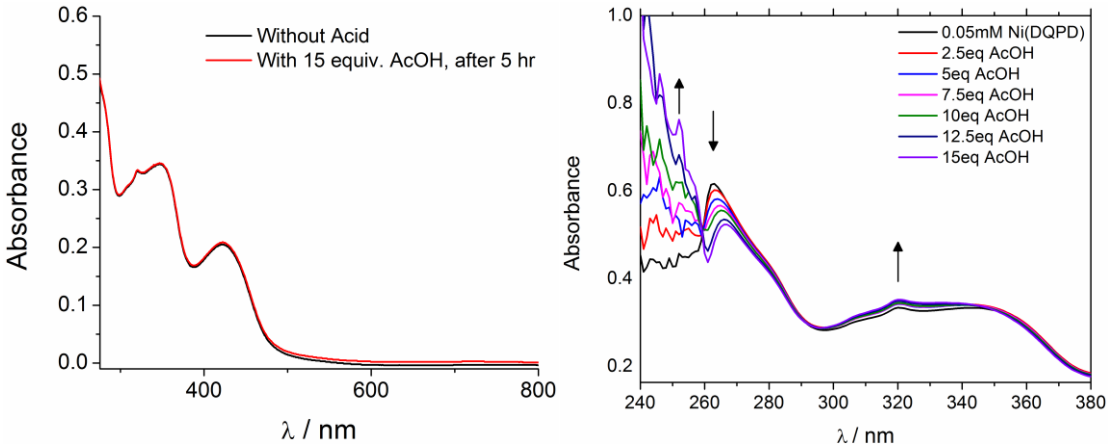

Figure S30. The UV-Visible spectrum of the 0.05 mM **Ni(DQPD)** complex in DMF/H_2O (95:5, v/v) with addition of 15 equivalent of CH_3COOH (left). Acid titration of 0.05 mM **Ni(DQPD)** complex in DMF/H_2O (95:5, v/v) (right).

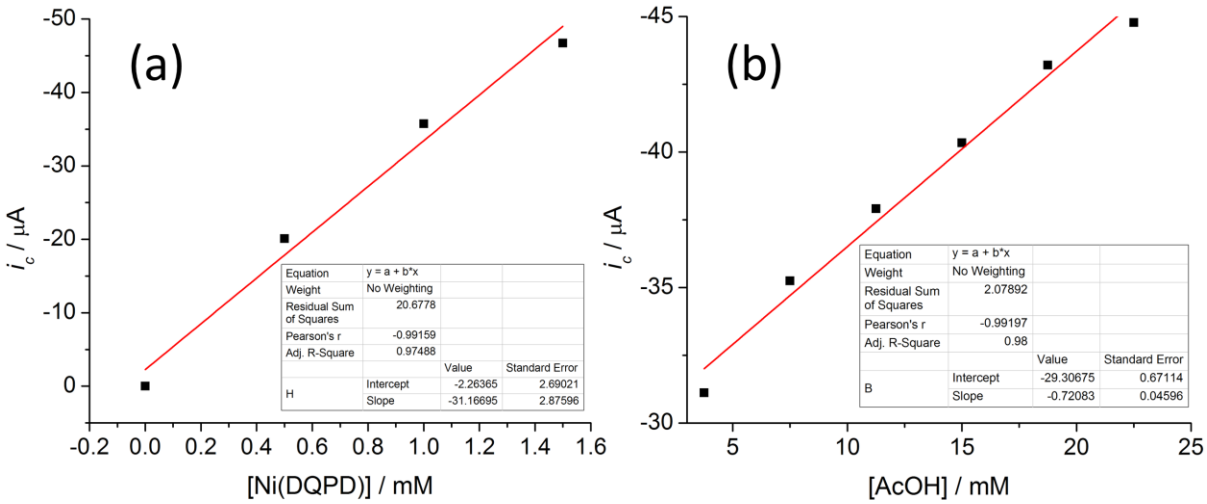

Figure S31. Dependence of catalytic current, i_c, (a) on metal concentration in presence of 15 equivalent of acetic acid. (b) On acetic acid concentration for a catalyst concentration of 1.5 mM. The supporting electrolyte is 0.1 M TBAP, and the potential scan rate is 100 mV s^{-1}.

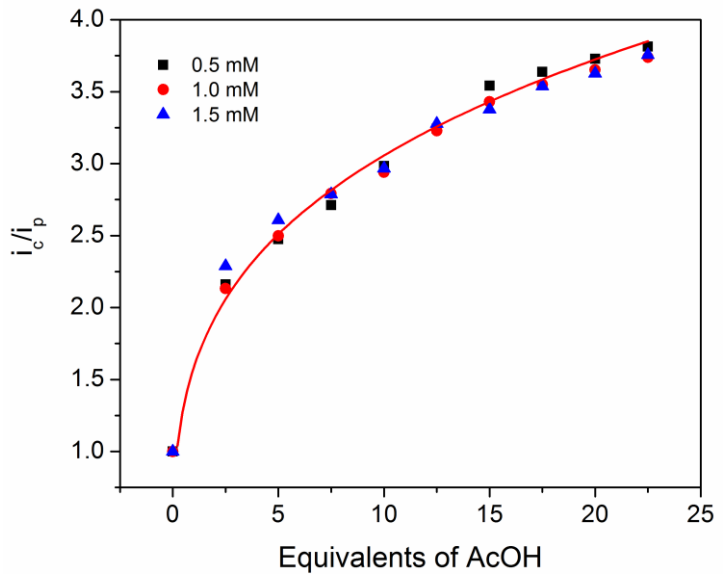

Figure S32. Dependence of i_c/i_p, on acetic acid concentration for three different concentrations of catalyst. Experiments were undertaken at three different catalyst concentrations: 0.5, 1.0 and 1.5 mM catalyst. The supporting electrolyte is 0.1 M TBAP, and the potential scan rate is 100 mV s^{-1}.

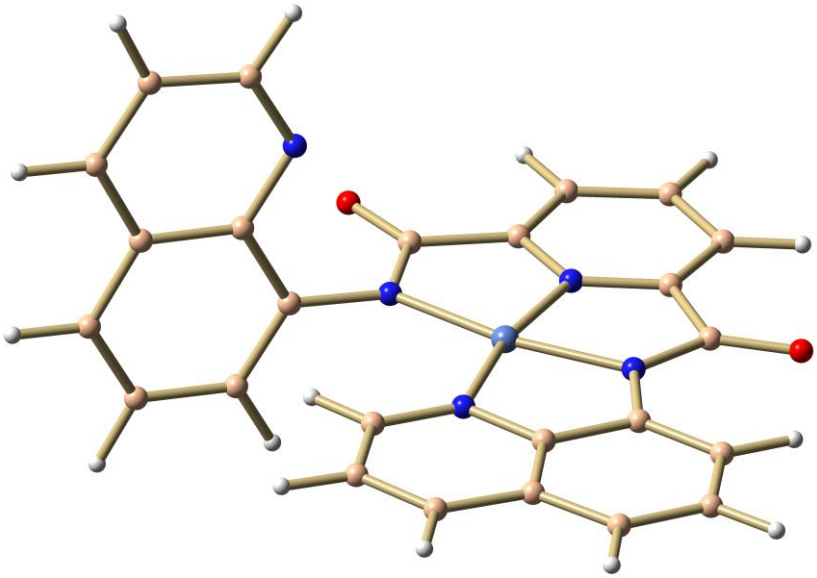

Figure S33. Optimized structure of **Ni(DQPD)**.

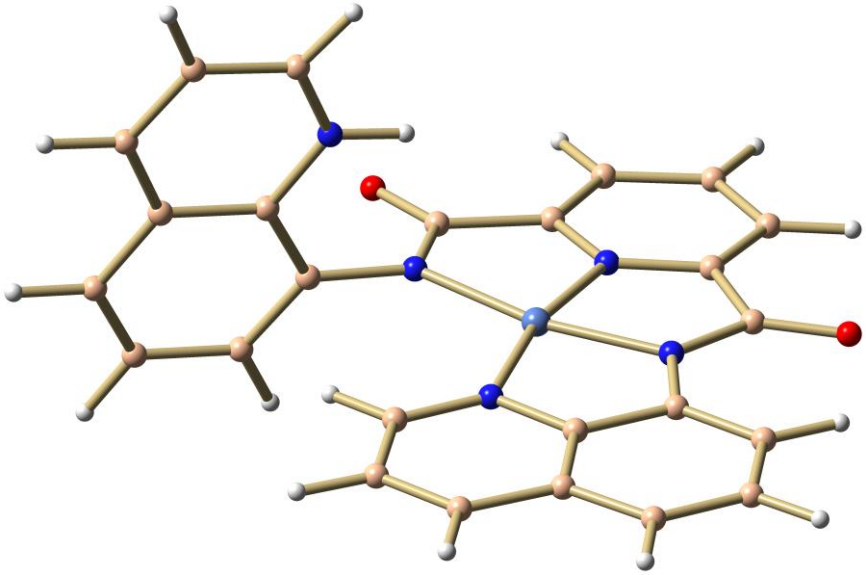

Figure S34. Optimized structure of **1** generated after protonation of **Ni(DQPD)**.

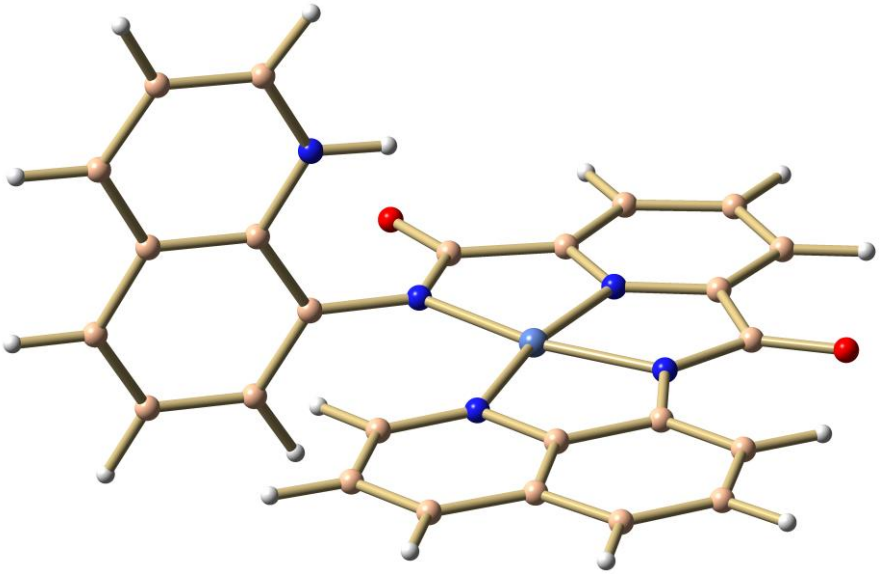

Figure S35. Optimized structure of **1a** generated after one electron reduction of **1**.

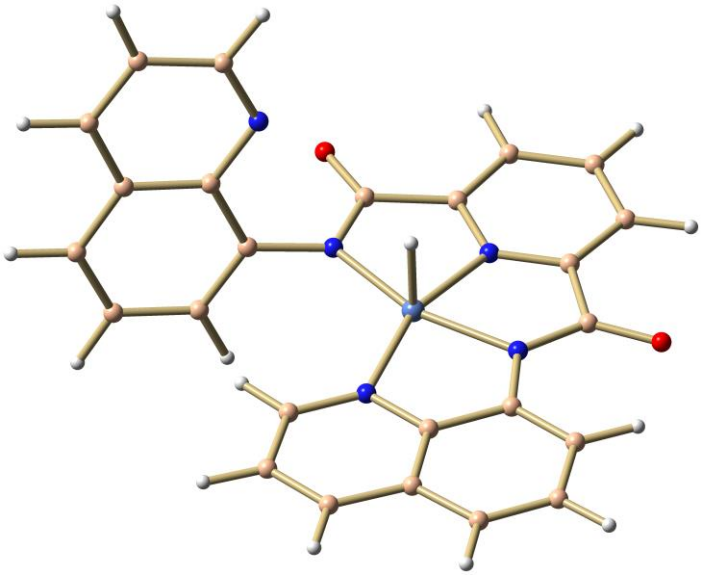

Figure S36. Optimized structure of **2a** generated after one electron reduction of **Ni^{II}(DQPD)** to **Ni^{I}(DQPD)** followed by protonation. The complex **2a** is energetically 40 kCal/mol less stable than **1a.**

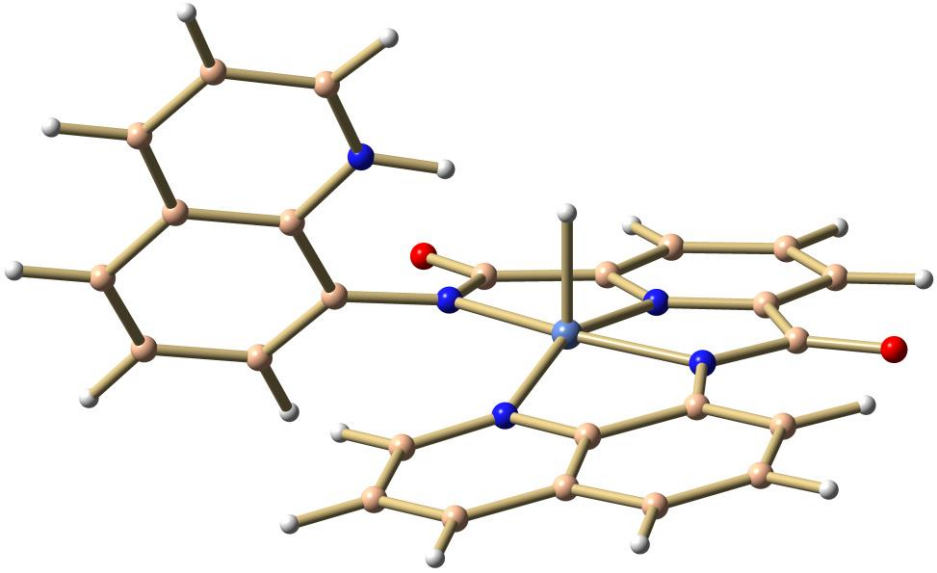

Figure S37. Optimized structure of **1b** generated after protonation of **1a**.

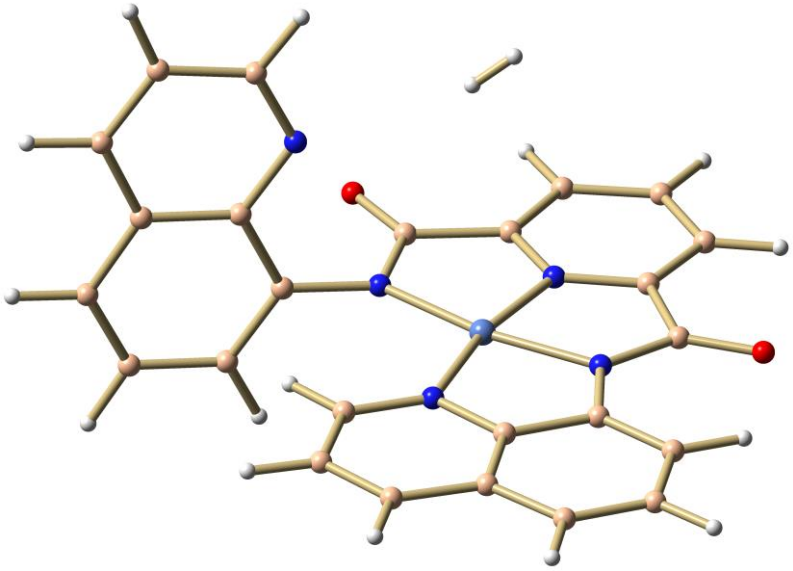

Figure S38. Optimized structure of **1c** generated after one electron reduction of **1b**. Upon one electron reduction to **1b**, wherein the hydrogen molecule formed and dissociated from the Ni atom generates the reduced complex **1c**.

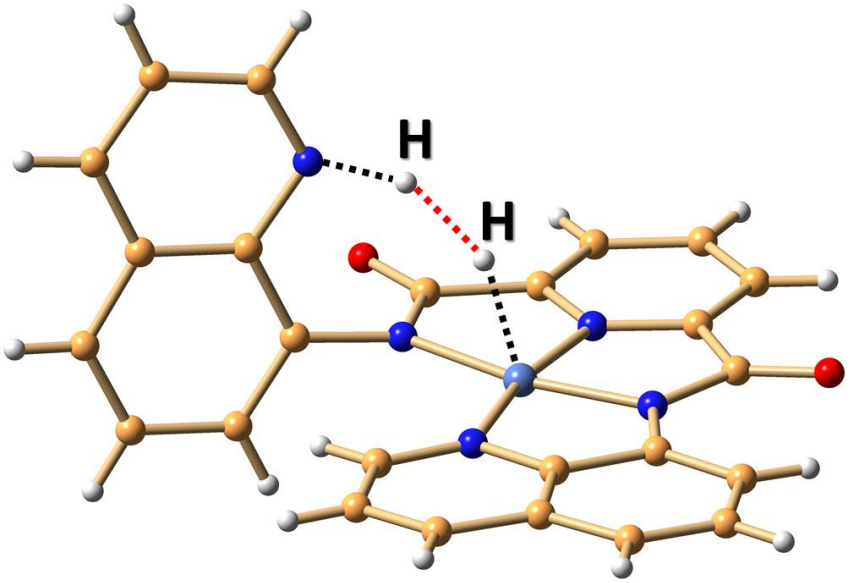

Figure S39. The transition state **TS1** identified by carrying out a synchronous transit-guided quasi-Newton (STQN) calculation using (**1b**) as a starting structure and the product as (**Intermediate**).

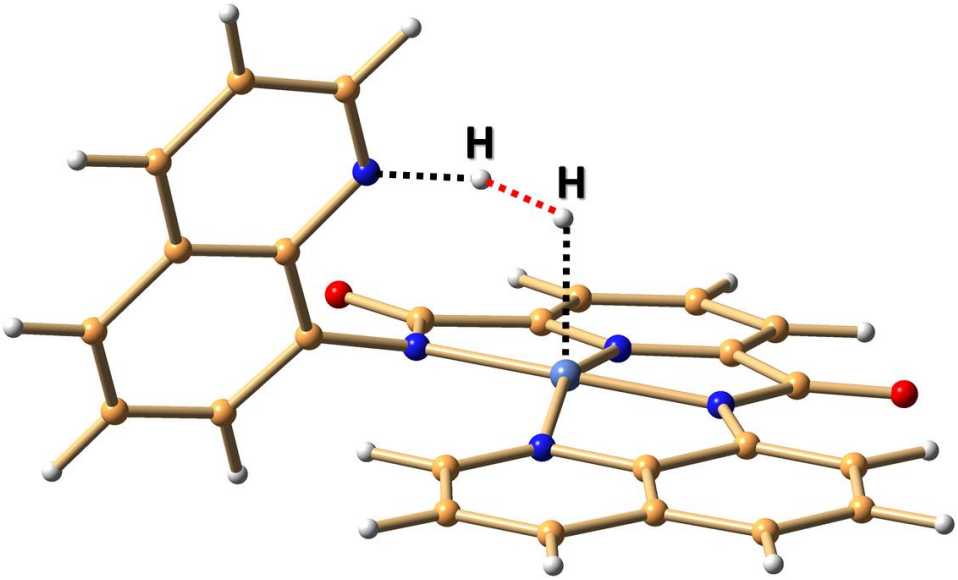

Figure S40. Structure of the intermediate.

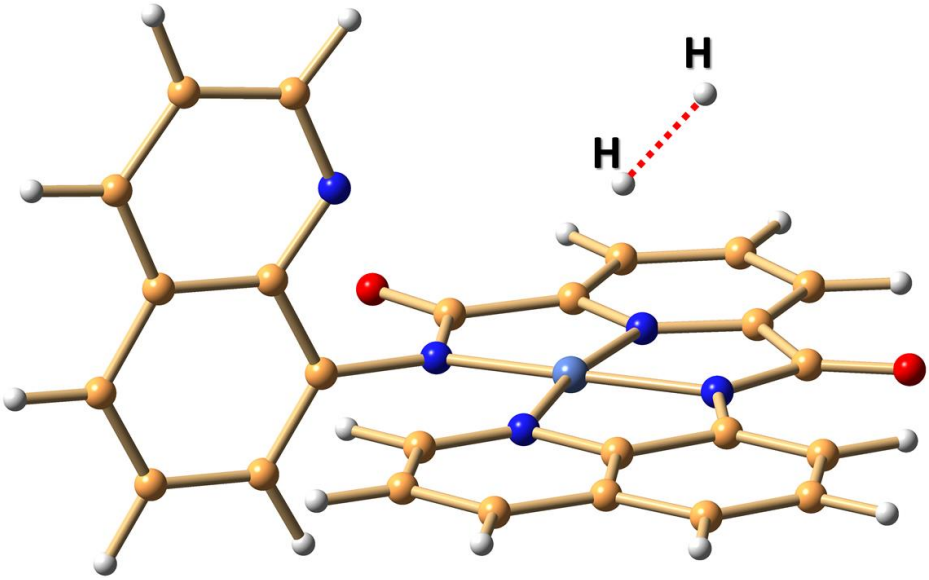

Figure S41. The transition state **TS2** identified by carrying out a synchronous transit-guided quasi-Newton (STQN) calculation using (**intermediate**) as a starting structure and the product as (**1c**).

Table S1. Crystal Data and Refinement Parameters of **Ni(DQPD)·H_2O**.

	Ni(DQPD)·H_2O
CCDC Number	CCDC 1401801
Empirical formula	$C_{25}H_{15}N_5NiO_2$
Formula weight	494.13
Temperature (K)	296(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	11.555(1)
b, Å	19.806(1)
c, Å	9.154(1)
α, deg	90
β, deg	94.097(3)
γ, deg	90
V, Å^3	2089.46
Z	4
D_{calc} (g cm^{-3})	1.414
μ, (mm^{-1})	0.950
[a]GOF on F^2	0.993
R [I>2σ(I)]	[b]R_1 = 0.0578, [c]wR_2 = 0.1267
R indices (all data)	[b]R_1 = 0.1413, [c]wR_2 = 0.1753

[a]GOF = $[\Sigma[w(F_0^2 - F_c^2)^2]/M - N]^{1/2}$ (M = number of reflections, N = number of parameters refined). [b]$R_1 = \Sigma ||F_0| - |F_c||/\Sigma|F_0|$. [c]$wR_2 = [\Sigma[w(F_0^2 - F_c^2)^2]/ \Sigma[w(F_0^2)^2]]$.

Table S2. XYZ coordinates for **Ni(DQPD)**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	28	0	1.102000	0.624000	5.869000
2	7	0	1.951000	-0.671000	4.909000

3	7	0	2.551000	1.706000	5.241000
4	7	0	-0.069000	-0.755000	6.273000
5	8	0	4.450000	1.553000	3.904000
6	8	0	-0.359000	-3.068000	6.047000
7	6	0	3.435000	1.073000	4.424000
8	6	0	1.454000	-1.925000	4.945000
9	6	0	3.067000	-0.360000	4.233000
10	6	0	3.718000	-1.333000	3.516000
11	1	0	4.476000	-1.125000	3.020000
12	6	0	0.231000	-2.012000	5.807000
13	6	0	2.088000	-2.935000	4.257000
14	1	0	1.754000	-3.803000	4.272000
15	6	0	3.229000	-2.632000	3.544000
16	1	0	3.673000	-3.304000	3.077000
17	6	0	-1.121000	-0.432000	7.145000
18	6	0	-3.083000	-0.669000	8.506000
19	1	0	-3.767000	-1.210000	8.831000
20	6	0	-1.070000	0.945000	7.514000
21	6	0	-3.035000	0.626000	8.894000
22	1	0	-3.666000	0.955000	9.492000
23	6	0	-2.026000	1.481000	8.392000
24	6	0	-0.008000	2.983000	7.263000
25	1	0	0.664000	3.504000	6.889000
26	6	0	-0.923000	3.593000	8.117000

27	1	0	-0.863000	4.504000	8.291000
28	6	0	-1.911000	2.850000	8.699000
29	1	0	-2.505000	3.246000	9.294000
30	6	0	-2.136000	-1.228000	7.630000
31	1	0	-2.194000	-2.121000	7.382000
32	6	0	2.887000	3.047000	5.587000
33	6	0	3.801000	3.317000	6.641000
34	6	0	4.102000	4.672000	6.962000
35	6	0	3.444000	5.708000	6.270000
36	1	0	3.612000	6.593000	6.501000
37	6	0	2.573000	5.433000	5.277000
38	1	0	2.156000	6.126000	4.821000
39	6	0	2.290000	4.086000	4.926000
40	1	0	1.690000	3.910000	4.237000
41	7	0	4.341000	2.259000	7.324000
42	6	0	5.033000	4.918000	7.975000
43	1	0	5.266000	5.789000	8.202000
44	7	0	-0.053000	1.692000	6.960000
45	6	0	5.195000	2.553000	8.289000
46	1	0	5.559000	1.850000	8.777000
47	6	0	5.589000	3.860000	8.627000
48	1	0	6.226000	4.003000	9.290000

Table S3. XYZ coordinates for **Ni(DQPDH) (1)**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	28	0	1.102000	0.624000	5.869000
2	7	0	1.951000	-0.671000	4.909000
3	7	0	2.551000	1.706000	5.241000
4	7	0	-0.069000	-0.755000	6.273000
5	8	0	4.450000	1.553000	3.904000
6	8	0	-0.359000	-3.068000	6.047000
7	6	0	3.435000	1.073000	4.424000
8	6	0	1.454000	-1.925000	4.945000
9	6	0	3.067000	-0.360000	4.233000
10	6	0	3.718000	-1.333000	3.516000
11	1	0	4.476000	-1.125000	3.020000
12	6	0	0.231000	-2.012000	5.807000
13	6	0	2.088000	-2.935000	4.257000
14	1	0	1.754000	-3.803000	4.272000
15	6	0	3.229000	-2.632000	3.544000
16	1	0	3.673000	-3.304000	3.077000
17	6	0	-1.121000	-0.432000	7.145000
18	6	0	-3.083000	-0.669000	8.506000
19	1	0	-3.767000	-1.210000	8.831000
20	6	0	-1.070000	0.945000	7.514000

21	6	0	-3.035000	0.626000	8.894000
22	1	0	-3.666000	0.955000	9.492000
23	6	0	-2.026000	1.481000	8.392000
24	6	0	-0.008000	2.983000	7.263000
25	1	0	0.664000	3.504000	6.889000
26	6	0	-0.923000	3.593000	8.117000
27	1	0	-0.863000	4.504000	8.291000
28	6	0	-1.911000	2.850000	8.699000
29	1	0	-2.505000	3.246000	9.294000
30	6	0	-2.136000	-1.228000	7.630000
31	1	0	-2.194000	-2.121000	7.382000
32	6	0	2.887000	3.047000	5.587000
33	6	0	3.801000	3.317000	6.641000
34	6	0	4.102000	4.672000	6.962000
35	6	0	3.444000	5.708000	6.270000
36	1	0	3.612000	6.593000	6.501000
37	6	0	2.573000	5.433000	5.277000
38	1	0	2.156000	6.126000	4.821000
39	6	0	2.290000	4.086000	4.926000
40	1	0	1.690000	3.910000	4.237000
41	7	0	4.341000	2.259000	7.324000
42	6	0	5.033000	4.918000	7.975000
43	1	0	5.266000	5.789000	8.202000
44	7	0	-0.053000	1.692000	6.960000

45	6	0	5.195000	2.553000	8.289000
46	1	0	5.559000	1.850000	8.777000
47	6	0	5.589000	3.860000	8.627000
48	1	0	6.226000	4.003000	9.290000
49	1	0	4.101402	1.313434	7.103781

Table S4. XYZ coordinates for **(1a)**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	28	0	1.102000	0.624000	5.869000
2	7	0	1.951000	-0.671000	4.909000
3	7	0	2.551000	1.706000	5.241000
4	7	0	-0.069000	-0.755000	6.273000
5	8	0	4.450000	1.553000	3.904000
6	8	0	-0.359000	-3.068000	6.047000
7	6	0	3.435000	1.073000	4.424000
8	6	0	1.454000	-1.925000	4.945000
9	6	0	3.067000	-0.360000	4.233000
10	6	0	3.718000	-1.333000	3.516000
11	1	0	4.476000	-1.125000	3.020000
12	6	0	0.231000	-2.012000	5.807000
13	6	0	2.088000	-2.935000	4.257000

14	1	0	1.754000	-3.803000	4.272000
15	6	0	3.229000	-2.632000	3.544000
16	1	0	3.673000	-3.304000	3.077000
17	6	0	-1.121000	-0.432000	7.145000
18	6	0	-3.083000	-0.669000	8.506000
19	1	0	-3.767000	-1.210000	8.831000
20	6	0	-1.070000	0.945000	7.514000
21	6	0	-3.035000	0.626000	8.894000
22	1	0	-3.666000	0.955000	9.492000
23	6	0	-2.026000	1.481000	8.392000
24	6	0	-0.008000	2.983000	7.263000
25	1	0	0.664000	3.504000	6.889000
26	6	0	-0.923000	3.593000	8.117000
27	1	0	-0.863000	4.504000	8.291000
28	6	0	-1.911000	2.850000	8.699000
29	1	0	-2.505000	3.246000	9.294000
30	6	0	-2.136000	-1.228000	7.630000
31	1	0	-2.194000	-2.121000	7.382000
32	6	0	2.887000	3.047000	5.587000
33	6	0	3.801000	3.317000	6.641000
34	6	0	4.102000	4.672000	6.962000
35	6	0	3.444000	5.708000	6.270000
36	1	0	3.612000	6.593000	6.501000
37	6	0	2.573000	5.433000	5.277000

38	1	0	2.156000	6.126000	4.821000
39	6	0	2.290000	4.086000	4.926000
40	1	0	1.690000	3.910000	4.237000
41	7	0	4.341000	2.259000	7.324000
42	6	0	5.033000	4.918000	7.975000
43	1	0	5.266000	5.789000	8.202000
44	7	0	-0.053000	1.692000	6.960000
45	6	0	5.195000	2.553000	8.289000
46	1	0	5.559000	1.850000	8.777000
47	6	0	5.589000	3.860000	8.627000
48	1	0	6.226000	4.003000	9.290000
49	1	0	4.101402	1.313434	7.103781

Table S5. XYZ coordinates for **(1b)**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	28	0	1.102000	0.624000	5.869000
2	7	0	1.951000	-0.671000	4.909000
3	7	0	2.551000	1.706000	5.241000
4	7	0	-0.069000	-0.755000	6.273000
5	8	0	4.450000	1.553000	3.904000
6	8	0	-0.359000	-3.068000	6.047000

7	6	0	3.435000	1.073000	4.424000
8	6	0	1.454000	-1.925000	4.945000
9	6	0	3.067000	-0.360000	4.233000
10	6	0	3.718000	-1.333000	3.516000
11	1	0	4.476000	-1.125000	3.020000
12	6	0	0.231000	-2.012000	5.807000
13	6	0	2.088000	-2.935000	4.257000
14	1	0	1.754000	-3.803000	4.272000
15	6	0	3.229000	-2.632000	3.544000
16	1	0	3.673000	-3.304000	3.077000
17	6	0	-1.121000	-0.432000	7.145000
18	6	0	-3.083000	-0.669000	8.506000
19	1	0	-3.767000	-1.210000	8.831000
20	6	0	-1.070000	0.945000	7.514000
21	6	0	-3.035000	0.626000	8.894000
22	1	0	-3.666000	0.955000	9.492000
23	6	0	-2.026000	1.481000	8.392000
24	6	0	-0.008000	2.983000	7.263000
25	1	0	0.664000	3.504000	6.889000
26	6	0	-0.923000	3.593000	8.117000
27	1	0	-0.863000	4.504000	8.291000
28	6	0	-1.911000	2.850000	8.699000
29	1	0	-2.505000	3.246000	9.294000
30	6	0	-2.136000	-1.228000	7.630000

31	1	0	-2.194000	-2.121000	7.382000
32	6	0	2.887000	3.047000	5.587000
33	6	0	3.801000	3.317000	6.641000
34	6	0	4.102000	4.672000	6.962000
35	6	0	3.444000	5.708000	6.270000
36	1	0	3.612000	6.593000	6.501000
37	6	0	2.573000	5.433000	5.277000
38	1	0	2.156000	6.126000	4.821000
39	6	0	2.290000	4.086000	4.926000
40	1	0	1.690000	3.910000	4.237000
41	7	0	4.341000	2.259000	7.324000
42	6	0	5.033000	4.918000	7.975000
43	1	0	5.266000	5.789000	8.202000
44	7	0	-0.053000	1.692000	6.960000
45	6	0	5.195000	2.553000	8.289000
46	1	0	5.559000	1.850000	8.777000
47	6	0	5.589000	3.860000	8.627000
48	1	0	6.226000	4.003000	9.290000
49	1	0	4.101402	1.313434	7.103781
50	1	0	1.893229	0.481124	7.075666

Table S6. XYZ coordinates for **(1b')**

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	28	0	1.102000	0.624000	5.869000
2	7	0	1.951000	-0.671000	4.909000
3	7	0	2.551000	1.706000	5.241000
4	7	0	-0.069000	-0.755000	6.273000
5	8	0	4.450000	1.553000	3.904000
6	8	0	-0.359000	-3.068000	6.047000
7	6	0	3.435000	1.073000	4.424000
8	6	0	1.454000	-1.925000	4.945000
9	6	0	3.067000	-0.360000	4.233000
10	6	0	3.718000	-1.333000	3.516000
11	1	0	4.476000	-1.125000	3.020000
12	6	0	0.231000	-2.012000	5.807000
13	6	0	2.088000	-2.935000	4.257000
14	1	0	1.754000	-3.803000	4.272000
15	6	0	3.229000	-2.632000	3.544000
16	1	0	3.673000	-3.304000	3.077000
17	6	0	-1.121000	-0.432000	7.145000
18	6	0	-3.083000	-0.669000	8.506000
19	1	0	-3.767000	-1.210000	8.831000
20	6	0	-1.070000	0.945000	7.514000
21	6	0	-3.035000	0.626000	8.894000
22	1	0	-3.666000	0.955000	9.492000

23	6	0	-2.026000	1.481000	8.392000
24	6	0	-0.008000	2.983000	7.263000
25	1	0	0.664000	3.504000	6.889000
26	6	0	-0.923000	3.593000	8.117000
27	1	0	-0.863000	4.504000	8.291000
28	6	0	-1.911000	2.850000	8.699000
29	1	0	-2.505000	3.246000	9.294000
30	6	0	-2.136000	-1.228000	7.630000
31	1	0	-2.194000	-2.121000	7.382000
32	6	0	2.887000	3.047000	5.587000
33	6	0	3.801000	3.317000	6.641000
34	6	0	4.102000	4.672000	6.962000
35	6	0	3.444000	5.708000	6.270000
36	1	0	3.612000	6.593000	6.501000
37	6	0	2.573000	5.433000	5.277000
38	1	0	2.156000	6.126000	4.821000
39	6	0	2.290000	4.086000	4.926000
40	1	0	1.690000	3.910000	4.237000
41	7	0	4.341000	2.259000	7.324000
42	6	0	5.033000	4.918000	7.975000
43	1	0	5.266000	5.789000	8.202000
44	7	0	-0.053000	1.692000	6.960000
45	6	0	5.195000	2.553000	8.289000
46	1	0	5.559000	1.850000	8.777000

47	6	0	5.589000	3.860000	8.627000
48	1	0	6.226000	4.003000	9.290000
49	1	0	4.101402	1.313434	7.103781
50	1	0	0.340426	1.161510	4.758330

Table S7. XYZ coordinates for (**1c**)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	28	0	1.102000	0.624000	5.869000
2	7	0	1.951000	-0.671000	4.909000
3	7	0	2.551000	1.706000	5.241000
4	7	0	-0.069000	-0.755000	6.273000
5	8	0	4.450000	1.553000	3.904000
6	8	0	-0.359000	-3.068000	6.047000
7	6	0	3.435000	1.073000	4.424000
8	6	0	1.454000	-1.925000	4.945000
9	6	0	3.067000	-0.360000	4.233000
10	6	0	3.718000	-1.333000	3.516000
11	1	0	4.476000	-1.125000	3.020000
12	6	0	0.231000	-2.012000	5.807000
13	6	0	2.088000	-2.935000	4.257000
14	1	0	1.754000	-3.803000	4.272000

15	6	0	3.229000	-2.632000	3.544000
16	1	0	3.673000	-3.304000	3.077000
17	6	0	-1.121000	-0.432000	7.145000
18	6	0	-3.083000	-0.669000	8.506000
19	1	0	-3.767000	-1.210000	8.831000
20	6	0	-1.070000	0.945000	7.514000
21	6	0	-3.035000	0.626000	8.894000
22	1	0	-3.666000	0.955000	9.492000
23	6	0	-2.026000	1.481000	8.392000
24	6	0	-0.008000	2.983000	7.263000
25	1	0	0.664000	3.504000	6.889000
26	6	0	-0.923000	3.593000	8.117000
27	1	0	-0.863000	4.504000	8.291000
28	6	0	-1.911000	2.850000	8.699000
29	1	0	-2.505000	3.246000	9.294000
30	6	0	-2.136000	-1.228000	7.630000
31	1	0	-2.194000	-2.121000	7.382000
32	6	0	2.887000	3.047000	5.587000
33	6	0	3.801000	3.317000	6.641000
34	6	0	4.102000	4.672000	6.962000
35	6	0	3.444000	5.708000	6.270000
36	1	0	3.612000	6.593000	6.501000
37	6	0	2.573000	5.433000	5.277000
38	1	0	2.156000	6.126000	4.821000

39	6	0	2.290000	4.086000	4.926000
40	1	0	1.690000	3.910000	4.237000
41	7	0	4.341000	2.259000	7.324000
42	6	0	5.033000	4.918000	7.975000
43	1	0	5.266000	5.789000	8.202000
44	7	0	-0.053000	1.692000	6.960000
45	6	0	5.195000	2.553000	8.289000
46	1	0	5.559000	1.850000	8.777000
47	6	0	5.589000	3.860000	8.627000
48	1	0	6.226000	4.003000	9.290000
49	1	0	3.699068	1.161785	7.098658
50	1	0	2.295563	0.632773	7.080789

Table S8. XYZ coordinates for (**1c'**)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	28	0	1.102000	0.624000	5.869000
2	7	0	1.951000	-0.671000	4.909000
3	7	0	2.551000	1.706000	5.241000
4	7	0	-0.069000	-0.755000	6.273000
5	8	0	4.450000	1.553000	3.904000
6	8	0	-0.359000	-3.068000	6.047000

7	6	0	3.435000	1.073000	4.424000
8	6	0	1.454000	-1.925000	4.945000
9	6	0	3.067000	-0.360000	4.233000
10	6	0	3.718000	-1.333000	3.516000
11	1	0	4.476000	-1.125000	3.020000
12	6	0	0.231000	-2.012000	5.807000
13	6	0	2.088000	-2.935000	4.257000
14	1	0	1.754000	-3.803000	4.272000
15	6	0	3.229000	-2.632000	3.544000
16	1	0	3.673000	-3.304000	3.077000
17	6	0	-1.121000	-0.432000	7.145000
18	6	0	-3.083000	-0.669000	8.506000
19	1	0	-3.767000	-1.210000	8.831000
20	6	0	-1.070000	0.945000	7.514000
21	6	0	-3.035000	0.626000	8.894000
22	1	0	-3.666000	0.955000	9.492000
23	6	0	-2.026000	1.481000	8.392000
24	6	0	-0.008000	2.983000	7.263000
25	1	0	0.664000	3.504000	6.889000
26	6	0	-0.923000	3.593000	8.117000
27	1	0	-0.863000	4.504000	8.291000
28	6	0	-1.911000	2.850000	8.699000
29	1	0	-2.505000	3.246000	9.294000
30	6	0	-2.136000	-1.228000	7.630000

31	1	0	-2.194000	-2.121000	7.382000
32	6	0	2.887000	3.047000	5.587000
33	6	0	3.801000	3.317000	6.641000
34	6	0	4.102000	4.672000	6.962000
35	6	0	3.444000	5.708000	6.270000
36	1	0	3.612000	6.593000	6.501000
37	6	0	2.573000	5.433000	5.277000
38	1	0	2.156000	6.126000	4.821000
39	6	0	2.290000	4.086000	4.926000
40	1	0	1.690000	3.910000	4.237000
41	7	0	4.341000	2.259000	7.324000
42	6	0	5.033000	4.918000	7.975000
43	1	0	5.266000	5.789000	8.202000
44	7	0	-0.053000	1.692000	6.960000
45	6	0	5.195000	2.553000	8.289000
46	1	0	5.559000	1.850000	8.777000
47	6	0	5.589000	3.860000	8.627000
48	1	0	6.226000	4.003000	9.290000
49	1	0	4.101402	1.313434	7.103781
50	1	0	0.340426	1.161510	4.758330

Table S9. XYZ coordinates for (**TS1**)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	28	0	0.676501	0.370518	-0.318562
2	7	0	0.942547	2.169326	-0.204829
3	7	0	-1.133701	0.899165	-0.647816
4	7	0	2.487884	0.302569	0.069218
5	8	0	-2.426469	2.823458	-0.855251
6	8	0	4.300223	1.643301	0.704048
7	6	0	-1.349745	2.241672	-0.672999
8	6	0	2.173220	2.615612	0.122421
9	6	0	-0.093294	2.998551	-0.401230
10	6	0	0.097324	4.354778	-0.306715
11	1	0	-0.605011	4.941613	-0.468564
12	6	0	3.135020	1.485458	0.332265
13	6	0	2.402608	3.967267	0.248161
14	1	0	3.247001	4.287540	0.470941
15	6	0	1.353373	4.836788	0.035796
16	1	0	1.489837	5.753766	0.121451
17	6	0	3.041822	-0.981635	0.193278
18	6	0	4.652026	-2.724210	0.551901
19	1	0	5.528392	-2.972693	0.742693

20	6	0	2.056688	-1.984920	-0.047183
21	6	0	3.726679	-3.691858	0.358870
22	1	0	3.966845	-4.586250	0.438799
23	6	0	2.393623	-3.345680	0.036018
24	6	0	-0.131146	-2.456741	-0.626020
25	1	0	-0.986352	-2.174190	-0.853373
26	6	0	0.124182	-3.824522	-0.574820
27	1	0	-0.548363	-4.432512	-0.779342
28	6	0	1.366426	-4.272455	-0.223961
29	1	0	1.533318	-5.184301	-0.157929
30	6	0	4.337618	-1.355989	0.475834
31	1	0	4.994120	-0.713960	0.614114
32	6	0	-2.298794	0.087762	-0.770608
33	6	0	-3.112735	-0.188888	0.360840
34	6	0	-4.263178	-1.013132	0.197225
35	6	0	-4.532137	-1.580700	-1.063985
36	1	0	-5.262429	-2.147371	-1.165809
37	6	0	-3.743841	-1.313321	-2.125782
38	1	0	-3.940160	-1.684280	-2.953986
39	6	0	-2.612719	-0.466220	-1.981974
40	1	0	-2.079187	-0.287056	-2.722879
41	7	0	-2.744086	0.331961	1.573386
42	6	0	-5.073747	-1.242081	1.312576
43	1	0	-5.841016	-1.762299	1.240950

44	7	0	0.791646	-1.539860	-0.364681
45	6	0	-3.534207	0.060469	2.597583
46	1	0	-3.292019	0.389289	3.433090
47	6	0	-4.717441	-0.694159	2.506909
48	1	0	-5.255255	-0.818112	3.256027
49	1	0	-1.525982	0.759592	1.563916
50	1	0	-0.151591	0.309442	1.165902

Table S10. XYZ coordinates for (**TS2**)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	28	0	0.691363	0.360175	-0.227619
2	7	0	1.368757	2.042507	-0.131182
3	7	0	-0.947419	1.178892	-0.641017
4	7	0	2.456866	-0.111129	0.071065
5	8	0	-1.917249	3.345616	-0.760537
6	8	0	4.626398	0.763576	0.459586
7	6	0	-0.931242	2.533482	-0.583319
8	6	0	2.696803	2.237096	0.108116
9	6	0	0.461464	3.038047	-0.296043
10	6	0	0.894251	4.369162	-0.200108
11	1	0	0.179832	5.171066	-0.321029

12	6	0	3.415010	0.893754	0.234648
13	6	0	3.177266	3.534534	0.206039
14	1	0	4.229154	3.711337	0.392228
15	6	0	2.259727	4.610966	0.054108
16	1	0	2.620936	5.637901	0.133753
17	6	0	2.704490	-1.498431	0.112403
18	6	0	3.901070	-3.603389	0.312186
19	1	0	4.845156	-4.118705	0.474069
20	6	0	1.493205	-2.250111	-0.105269
21	6	0	2.743994	-4.346932	0.108427
22	1	0	2.777208	-5.428470	0.112123
23	6	0	1.502145	-3.682608	-0.106962
24	6	0	-0.832166	-2.174966	-0.512964
25	1	0	-1.742671	-1.585990	-0.679182
26	6	0	-0.895031	-3.587638	-0.526468
27	1	0	-1.854297	-4.068389	-0.698123
28	6	0	0.257965	-4.340031	-0.326365
29	1	0	0.216289	-5.427483	-0.335115
30	6	0	3.900940	-2.177154	0.316684
31	1	0	4.823830	-1.622424	0.476704
32	6	0	-2.233436	0.467440	-0.828710
33	6	0	-2.988201	0.192155	0.328895
34	6	0	-4.267174	-0.478576	0.214099
35	6	0	-4.731537	-0.841704	-1.081943

36	1	0	-5.691164	-1.339256	-1.167895
37	6	0	-3.967241	-0.559860	-2.216825
38	1	0	-4.332016	-0.828455	-3.207697
39	6	0	-2.704666	0.106178	-2.084437
40	1	0	-2.100195	0.351910	-2.953658
41	7	0	-2.451775	0.564795	1.478518
42	6	0	-4.951864	-0.705644	1.431325
43	1	0	-5.917601	-1.202877	1.418769
44	7	0	0.322533	-1.506083	-0.309835
45	6	0	-3.108015	0.333588	2.654580
46	1	0	-2.611939	0.651093	3.580803
47	6	0	-4.369677	-0.291281	2.655776
48	1	0	-4.875663	-0.455578	3.607191
49	1	0	0.899714	1.025266	2.020479
50	1	0	1.690868	0.719272	3.447443

Table S11. Selected bond distances (Å) and angles (°) in optimized **Ni(DQPD)·H_2O**.

Bond distances	**Distances (Å)**	**Bond Angle**	**Angles** (°)
Ni−N1	1.915(3)	N1−Ni−N2	82.9(1)
Ni−N2	1.822(2)	N1−Ni−N3	165.9(1)
Ni−N3	1.854(3)	N1−Ni−N4	109.2(1)
Ni−N4	1.914(4)	N2−Ni−N3	83.1(1)
		N2−Ni−N4	167.9(2)
		N3−Ni−N4	84.8(1)

Table S12. Selected bond distances (Å) and angles (°) in **Ni(DQPD)**.

Bond distances	**Distances (Å)**	**Bond Angle**	**Angles** (°)
Ni−N1	1.944	N1−Ni−N2	83.0
Ni−N2	1.851	N1−Ni−N3	165.8
Ni−N3	1.891	N1−Ni−N4	109.1
Ni−N4	1.940	N2−Ni−N3	82.8
		N2−Ni−N4	167.9
		N3−Ni−N4	85.1

Table S13. Selected bond distances (Å) and angles (°) in optimized **1**.

Bond distances	**Distances (Å)**	**Bond Angle**	**Angles** (°)
Ni−N1	1.959	N1−Ni−N2	82.8
Ni−N2	1.854	N1−Ni−N3	165.5
Ni−N3	1.887	N1−Ni−N4	109.3
Ni−N4	1.939	N2−Ni−N3	82.9
		N2−Ni−N4	167.8
		N3−Ni−N4	85.1

Table S14. Selected bond distances (Å) and angles (°) in optimized **1a**.

Bond distances	**Distances (Å)**	**Bond Angle**	**Angles** (°)
Ni−N1	1.945	N1−Ni−N2	83.1
Ni−N2	1.851	N1−Ni−N3	166.0
Ni−N3	1.893	N1−Ni−N4	108.9
Ni−N4	1.939	N2−Ni−N3	82.9
		N2−Ni−N4	167.9
		N3−Ni−N4	85.1

Table S15. Selected bond distances (Å) and angles (°) in optimized **1b**.

Bond distances	**Distances (Å)**	**Bond Angle**	**Angles** (°)
Ni−N1	1.942	N1−Ni−N2	83.0
Ni−N2	1.890	N1−Ni−N3	165.5
Ni−N3	1.874	N1−Ni−N4	108.9
Ni−N4	1.998	N2−Ni−N3	82.6
Ni−H	1.619	N2−Ni−N4	159.6
		N3−Ni−N4	84.4

Table S16. Selected bond distances (Å) and angles (°) in optimized **1c**.

Bond distances	**Distances (Å)**	**Bond Angle**	**Angles** (°)
Ni−N1	1.933	N1−Ni−N2	83.3
Ni−N2	1.849	N1−Ni−N3	166.1
Ni−N3	1.889	N1−Ni−N4	109.0
Ni−N4	1.941	N2−Ni−N3	82.8
H−H	0.747	N2−Ni−N4	167.8
		N3−Ni−N4	84.9

Table S17. Selected bond distances (Å) and angles (°) in optimized **2a**.

Bond distances	**Distances (Å)**	**Bond Angle**	**Angles** (°)
Ni−N1	1.973	N1−Ni−N2	81.1
Ni−N2	1.977	N1−Ni−N3	161.2
Ni−N3	1.974	N1−Ni−N4	116.5
Ni−N4	2.070	N2−Ni−N3	80.3
Ni−H	1.450	N2−Ni−N4	161.6
		N3−Ni−N4	82.3

Table S18. Selected bond distances (Å) and angles (°) in the transition state.

Bond distances	**Distances (Å)**	**Bond Angle**	**Angles** (°)
Ni−N1	1.960	N1−Ni−N2	83.2
Ni−N2	1.865	N1−Ni−N3	164.8
Ni−N3	1.902	N1−Ni−N4	108.3
Ni−N4	2.199	N2−Ni−N3	82.4
Ni−H	1.651	N2−Ni−N4	139.7
H−H	1.318	N3−Ni−N4	80.4