Supporting Information

A family of molecular nickel hydrogen evolution catalysts providing tunable overpotentials using ligand-centered proton-coupled electron transfer paths

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Experimental Section

Materials

All solvents and reagents were of the highest qualities available and were used as received. $Na_2[Ni(dcpdt)_2]•4H_2O$[1] (dcpdt = 5,6-dicyanopyrazine-2,3-dithiolate) and pyrido-[2,3-*b*]pyrazine-2,3-dithiol ($pypzdtH_2$)[2] were prepared as previously described.

Measurements

^{1}H NMR spectra were acquired on a JEOL JNM-ESA 600 spectrometer. ESI-TOF mass spectra were recorded on a JEOL JMS-T100CS spectrometer. Cyclic voltammetry (CV), square-wave voltammetry (SWV), and the bulk electrolysis were performed on an ALS 602DKM electrochemical analyzer (BAS). Linear sweep voltammetry (LSV) was performed on an ALS 700E electrochemical analyzer (BAS) and an RRDE-3A rotating ring disk electrode apparatus (BAS). For the experiments performed in aqueous solutions, a glassy carbon (GC) working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE; 0.241 V vs. NHE) were employed. For the experiments performed in organic solutions, a GC working electrode (5 mmϕ), a platinum wire counter electrode and an Ag/Ag^+ reference electrode (0.249 V vs SCE) were employed, where $TBAPF_6$ (tetra(n-butyl)ammonium hexafluorophosphate; 0.1 M) was used as a supporting electrolyte, and all the potentials reported are given relative to the Fc/Fc^+ couple (Fc/Fc^+ = 0.155 vs SCE). The bulk electrolysis was carried out by an H-type cell (VB-9) purchased from EC Frontier, using a GC rod working electrode (5 mm Φ, The Nilaco Corporation), a platinum mesh counter electrode, and an SCE. The working compartment was separated from the counter compartment using a cation exchange membrane (Selemion^{TM} CMD, AGC Engineering). The time-course of H_2 evolution during the bulk electrolysis was monitored using the automated system developed in our group. These experiments adopted the continuous Ar-flow method (10 mL min^{-1}) with the vent introduced into the auto sampler for the gas chromatographic analysis, as described elsewhere.[3] The pH measurements were performed using a DKK-TOA HM-25R pH meter.

Synthesis

Preparation of $Na_2[Ni(pypzdt)_2]$•$6H_2O$

The water-soluble sodium salt of $[Ni(pypzdt)_2]^{2-}$ was prepared according to the method reported for $[NBu_4]_2[Ni(pypzdt)_2]$,[2] with minor modifications as follows. To a solution of pypydtH_2 (1.82 g, 9.32 mmol) and NaOH (821 mg, 20.5 mmol) in methanol (200 mL) was added $NiCl_2 \cdot 6H_2O$ (1.11 g, 4.67 mmol), followed by stirring it for 30 min at room temperature. After the resulting dark purple mixture was filtered off, the filtrate was evaporated to a total volume of ca. 20 mL. The dark purple product deposited by adding diethyl ether was collected by filtration, and was redissolved in acetonitrile (500 mL) followed by filtration for the removal of insoluble materials. The filtrate was evaporated to dryness. The solid was redissolved in hot water (500 mL) followed by filtration for the removal of insoluble materials. The filtrate was evaporated to dryness to afford the final product as a dark purple powder (yield: 2.23 g, 3.78 mmol, 81%). ^{1}H NMR (600 MHz, DMSO-d6 (DMSO = dimethylsulfoxide)): δ = 8.44 (d, J = 6.0 Hz, 2H), 7.86 (d, J = 12 Hz, 2H), 7.24 (m, 2H). Anal. Calcd. for $C_{15}H_6N_6Na_2NiS_4 \cdot 6H_2O$ (f.w. 599.25): C, 28.06; H, 3.03; N, 14.02; Found: C, 28.05; H, 3.20; N, 13.72. ESI-TOF MS (negative ion, MeOH) 466.81 m/z (Na[**M**]$^-$).

Preparation of quinoxaline-2,3-dithiol (qdtH$_2$)

A suspension of thiourea (3.00 g, 39.4 mmol) and 2,3-dichloro quinoxaline (1.43 g, 7.36 mmol) in ethanol (25 mL) was refluxed for 1 h and cooled to room temperature. The solution was evaporated to a total volume of ca. 5 mL, followed by addition of an aqueous solution (50 mL) of NaOH (8.53 g, 213 mmol). The solution was refluxed for 30 min. After the solution was cooled to room temperature, the brown solution was filtered and the filtrate was acidified with acetic acid (ca. 15 mL) to give the product as a brown solid, which was collected by filtration, washed with water, and dried *in vacuo* (yield: 1.36 g, 7.02 mmol, 95%). ^{1}H NMR (600 MHz, DMSO-d6): δ = 14.28 (s, 2H), 7.43 (m, 2H), 7.29 (m, 2H).

Preparation of $Na_2[Ni(qdt)_2]$•$6H_2O$

This was prepared in the same manner as $Na_2[Ni(pypzdt)_2]$•$6H_2O$ using $NiCl_2 \cdot 6H_2O$ (367 mg, 1.54 mmol) and $qdtH_2$ (600 mg, 3.09 mmol) to afford the product as a brown powder (yield: 850 mg, 86%). ^1H NMR (600 MHz, DMSO-d6): δ = 7.46 (m, 2H), 7.18 (m, 2H). Anal. Calcd. for $C_{16}H_8N_4Na_2NiS_4 \cdot 6H_2O$ (f.w. 597.27): C, 31.95; H, 3.40; N, 9.37; Found: C, 32.17; H, 3.38; N, 9.38. ESI-TOF MS (negative ion, MeOH) 442.92 m/z (H[**M**]$^-$).

Computational Method

In order to better understand the structural and spin-state candidates, density functional theory (DFT) calculations were performed using the Gaussian 09 package of programs.[4] The structures were fully optimized using the B3P86 density functional[5,6] with the effect of solvation in water taken into consideration using the conductor-like polarizable continuum model (C-PCM) method.[7,8] The 6-311+G(d,p) basis set was applied to all atoms. The use of B3P86 functional was reported to show good consistency with theoretical and experimental results for the 1st row transition metal complexes.[9-12]

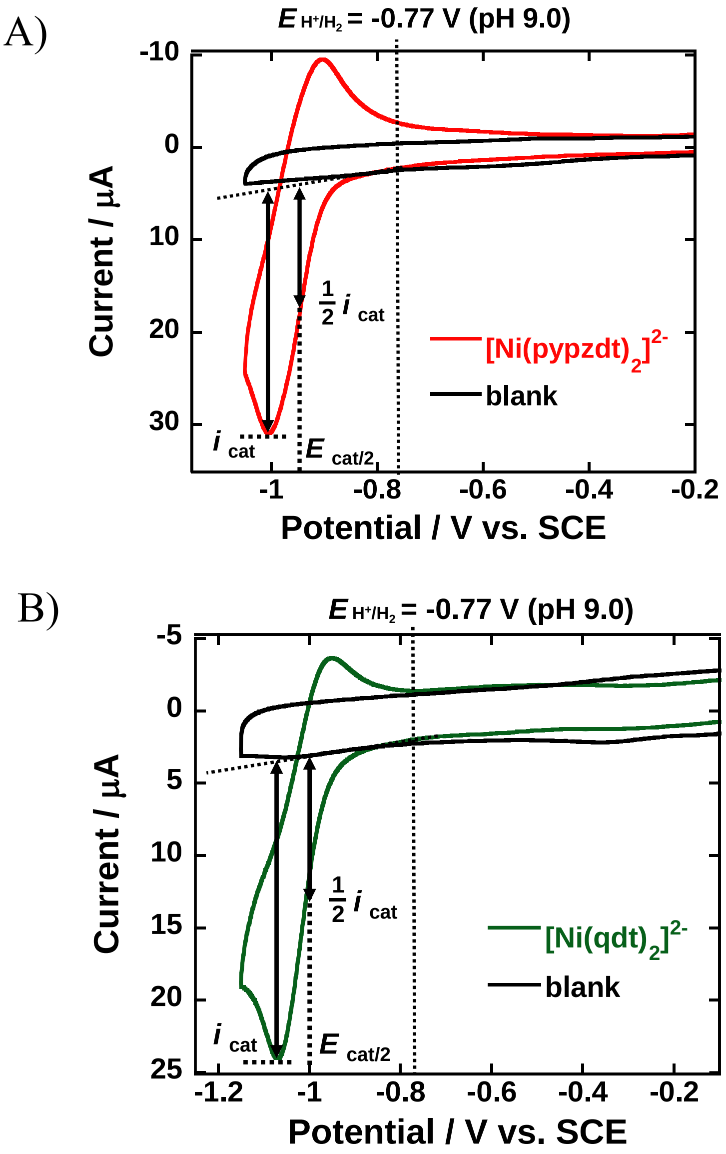


Fig. S1 CVs for an aqueous borate buffer solution (pH = 9.0; 0.1 M) of A) $Na_2[Ni(pypzdt)_2]\bullet 6H_2O$ (0.5 mM) and B) $Na_2[Ni(qdt)_2]\bullet 6H_2O$ containing NaCl (0.1 M) at room temperature under Ar atmosphere, recorded at a sweep rate of 100 mV s^{-1}. The overpotentials ($\eta(E_{cat/2})$'s) are determined as illustrated in these figures.

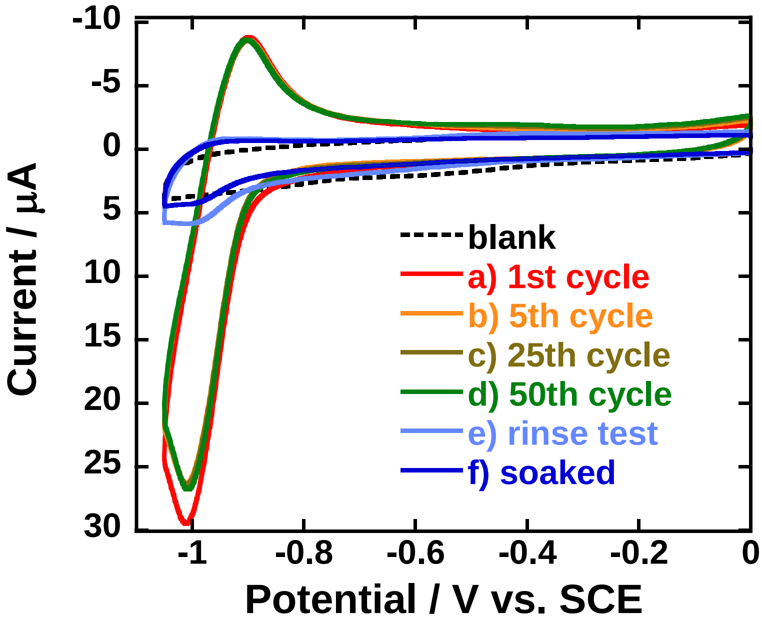
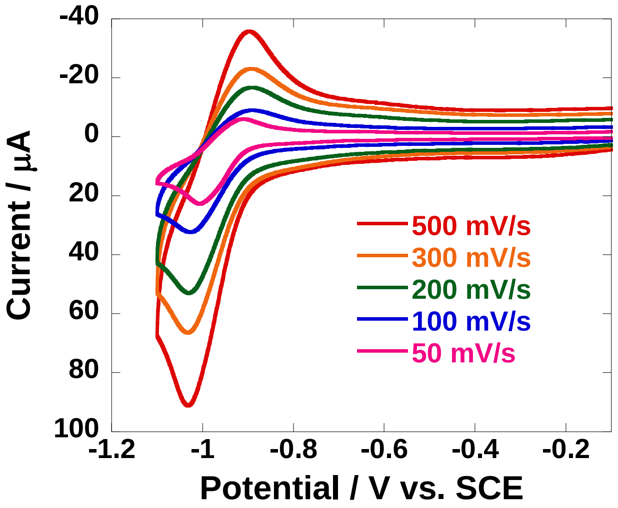


Fig. S2 CVs with use of a GC working electrode for an aqueous borate buffer solution (0.1 M; pH = 9.0) of $Na_2[Ni(pypzdt)_2]\cdot 6H_2O$ (0.5 mM) in the presence of NaCl (0.1 M), where 1st, 5th, 25th and 50th cycles are only shown. The e-labeled CV shows the result of the rinse test after the d-labeled scan, recorded after replacing the electrolysis solution with the same buffer solution free of the catalyst. The f-labeled CV was recorded by the same GC electrode which was preliminary soaked in a catalyst solution, where the measurement was carried out using the same buffer solution free of the catalyst. All the CVs are recorded at a sweep rate of 100 mV/s, under Ar atmosphere at room temperature.

A)



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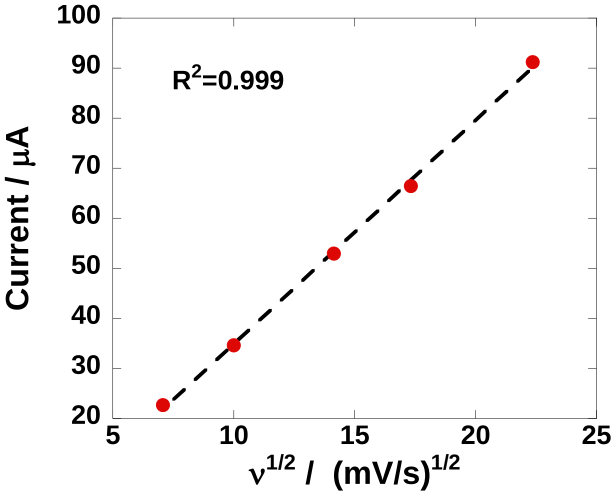


Fig. S3 A) CVs for an aqueous borate buffer solution (pH = 9.0; 0.1 M) of $Na_2[Ni(pypzdt)_2]\cdot 6H_2O$ (0.5 mM) containing NaCl (0.1 M), recorded at various sweep rates (50-500 mV/s) at room temperature under Ar atmosphere. B) i_{cat} versus $v^{1/2}$, where the i_{cat} values are obtained from the peak currents shown in Fig. S3A.

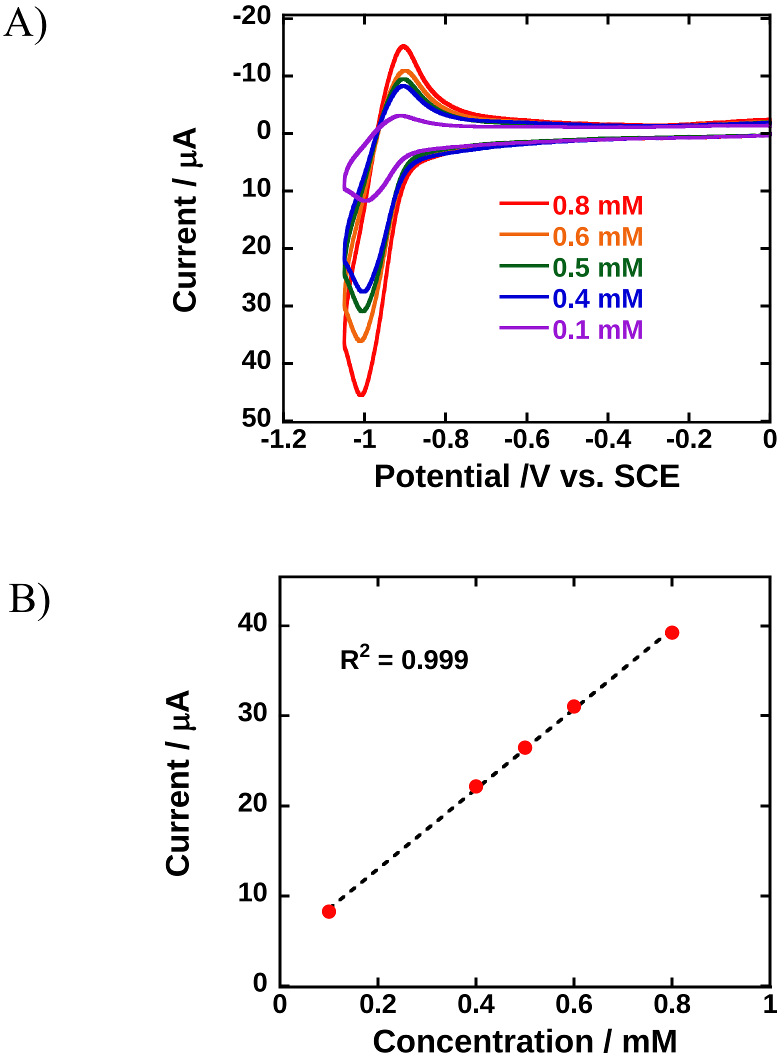


Fig. S4 A) CVs for an aqueous borate buffer solution (pH = 9.0; 0.1 M) of $Na_2[Ni(pypzdt)_2]•6H_2O$ at various concentrations (0.1-0.8 mM) containing NaCl (0.1 M), recorded at a sweep rate of 100 mV s^{-1} at room temperature under Ar atmosphere. B) i_{cat} versus the concentration of $Na_2[Ni(pypzdt)_2]•6H_2O$, where the i_{cat} values are obtained from the peak currents shown in Fig. S4A.

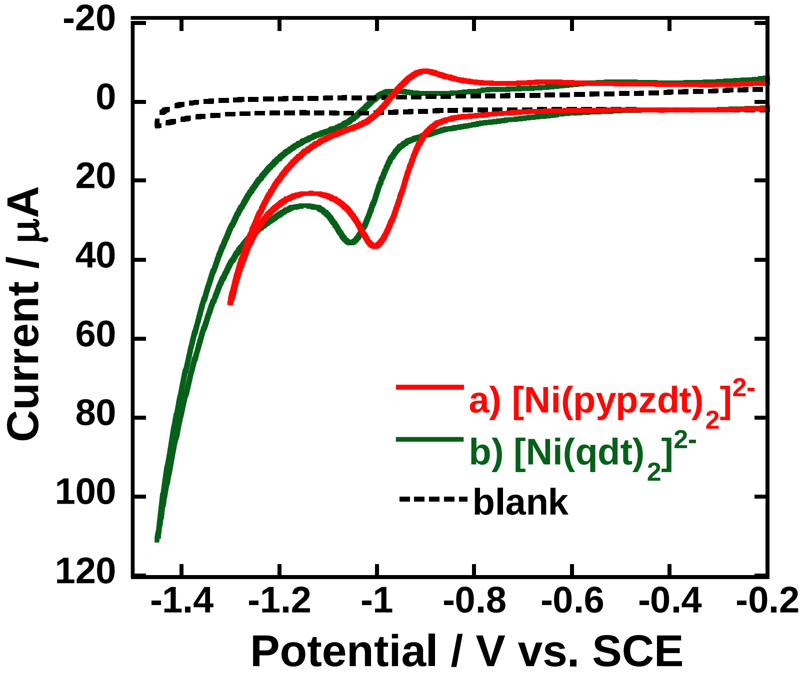


Fig. S5 CVs (sweep range: 0 V ~ -1.3 V vs. SCE) for an aqueous borate buffer solution (pH = 9.0; 0.1 M) of a) $Na_2[Ni(pypzdt)_2]•6H_2O$ and b) $Na_2[Ni(qdt)_2]•6H_2O$ (0.5 mM) containing NaCl (0.1 M) at room temperature under Ar atmosphere, recorded at a sweep rate of 100 mV s^{-1}.

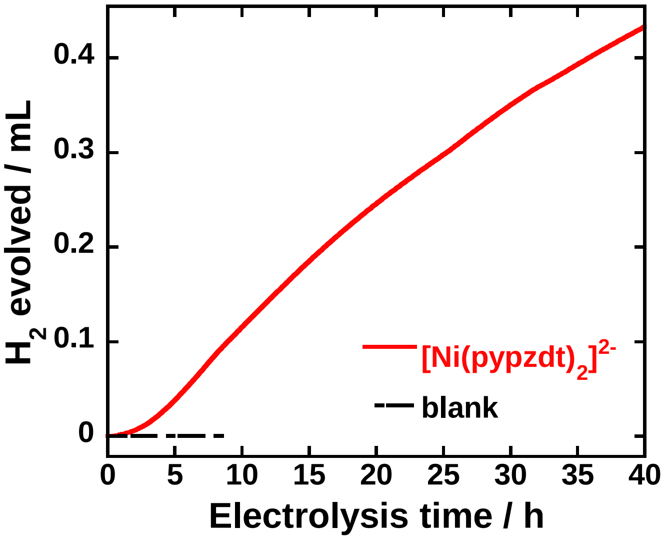


Fig. S6 Electrochemical H_2 evolution from water during the bulk electrolysis at -1.05 V vs. SCE of an aqueous borate buffer solution (pH 9.0; 0.1 M, 12 mL) containing NaCl (0.1 M) in the presence of $Na_2[Ni(pypzdt)_2]\cdot 6H_2O$ (1 μM) at room temperature under Ar. The working, counter, and reference electrodes were a GC rod, a Pt mesh, and an SCE, respectively.

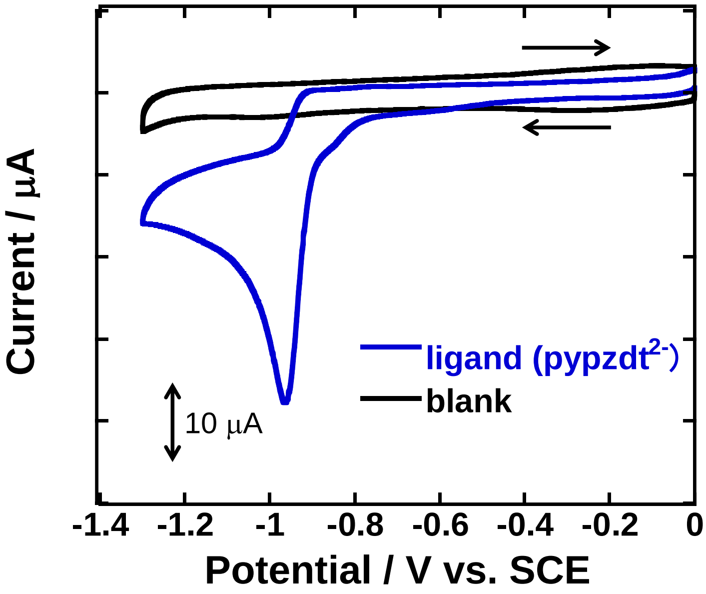


Fig. S7 A CV for an aqueous borate buffer solution (pH = 9.0; 0.1 M) of pypzdtH_2 (0.5 mM) containing NaCl (0.1 M) at room temperature under Ar atmosphere, recorded at a sweep rate of 100 mV s^{-1}.

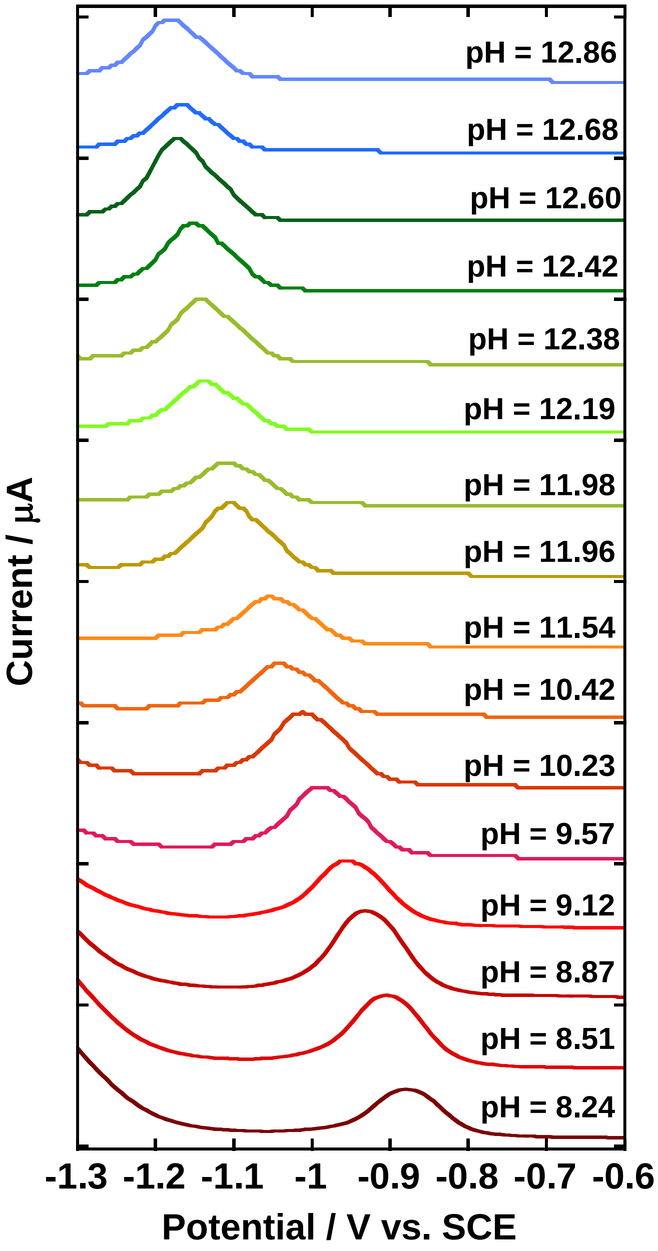


Fig. S8 SWVs for aqueous borate buffer solutions (0.1 M; pH = 8.24-12.86) of $Na_2[Ni(pypzdt)_2]•6H_2O$ containing NaCl (0.1 M) at room temperature under Ar atmosphere.

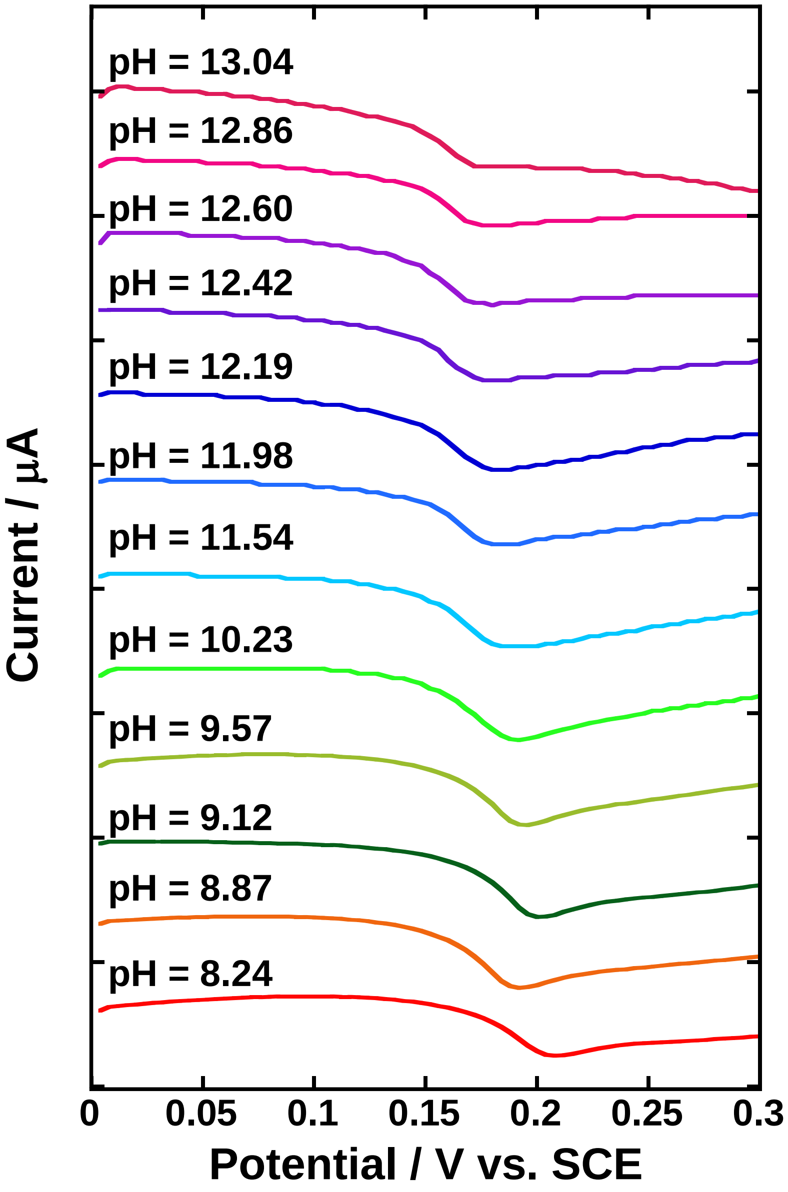


Fig. S9 SWVs for aqueous borate buffer solutions (0.1 M; pH = 8.24-13.04) of $Na_2[Ni(pypzdt)_2]\cdot 6H_2O$ containing NaCl (0.1 M) at room temperature under Ar atmosphere.

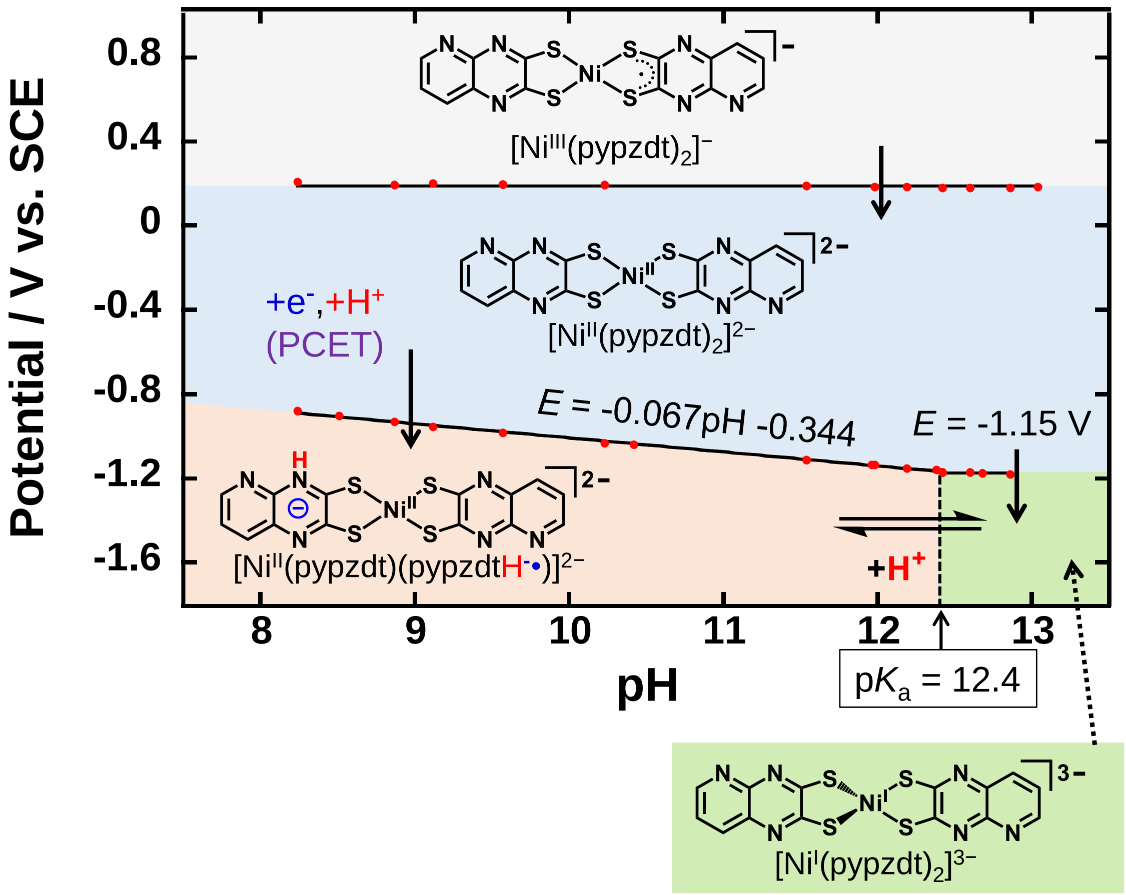


Fig. S10 Plots of the first reduction and oxidation potentials of [Ni(pypzdt)$_2$]$^{2-}$ as a function of pH ($8.2 < \mathrm{pH} < 13$), where potentials were determined by observing the SWVs of these complexes in aqueous buffer solutions at various pH conditions. See Figs. S8,S9 and Tables S1,S2 for datails.

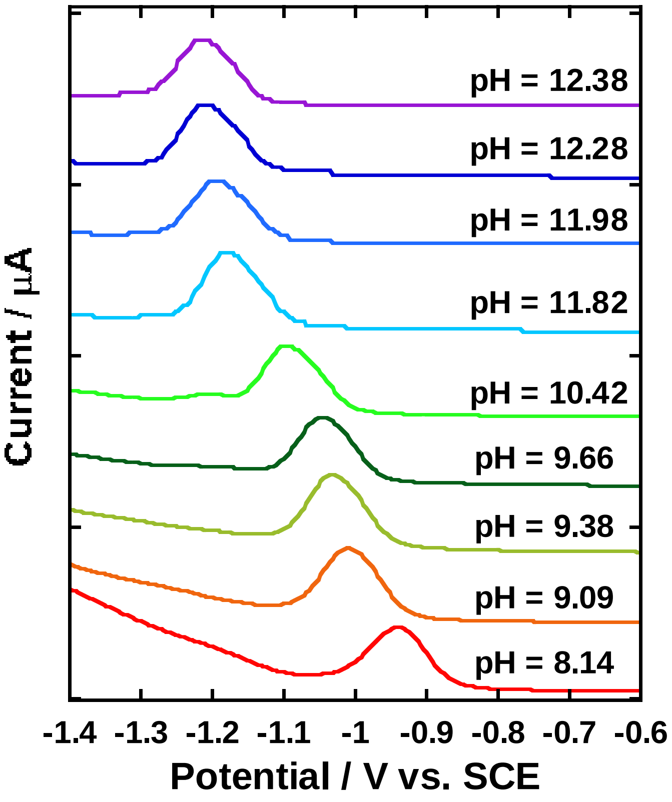


Fig. S11 SWVs for aqueous borate buffer solutions (0.1 M; pH = 8.14-12.38) of $Na_2[Ni(qdt)_2]•6H_2O$ containing NaCl (0.1 M) at room temperature under Ar atmosphere.

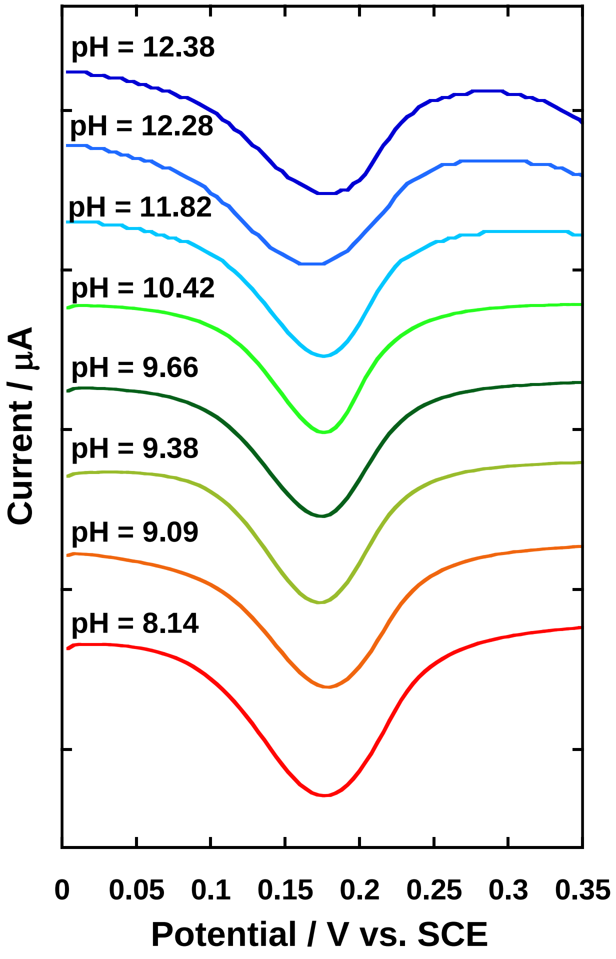


Fig. S12 SWVs for aqueous borate buffer solutions (0.1 M; pH = 8.14-12.38) of $Na_2[Ni(qdt)_2]\bullet 6H_2O$ containing NaCl (0.1 M) at room temperature under Ar atmosphere.

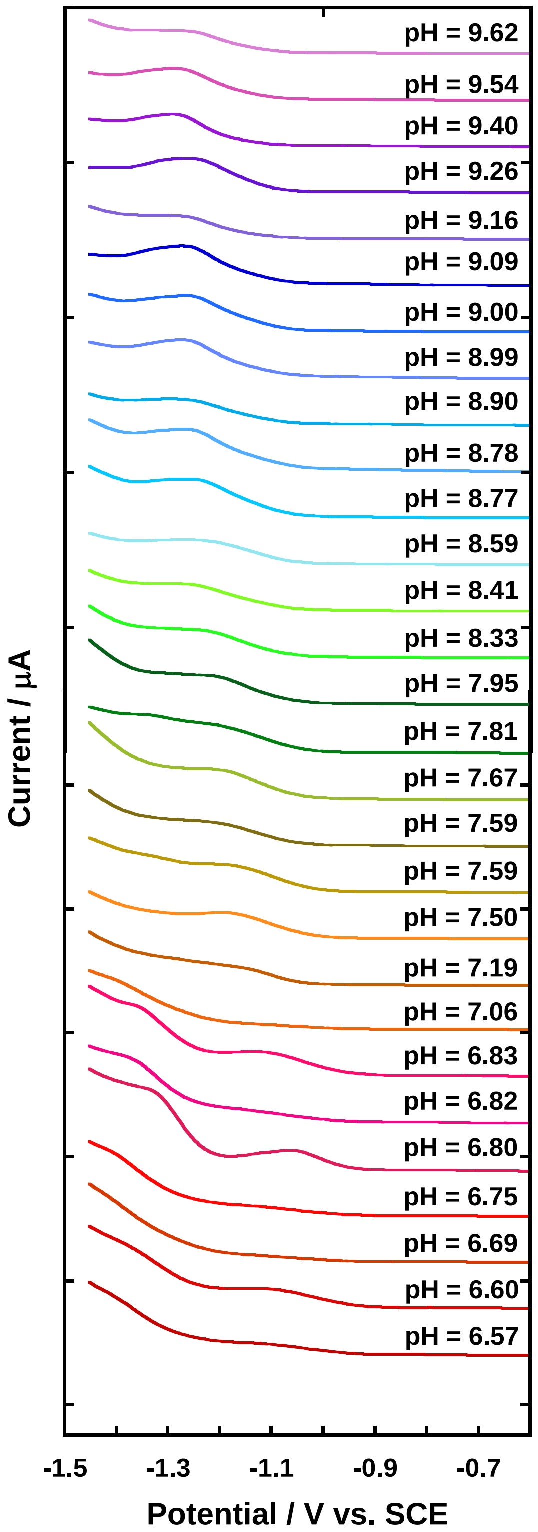


Fig. S13 SWVs for aqueous buffer solutions (0.1 M; pH = 6.57-9.62) of $Na_2[Ni(dcpdt)_2]•4H_2O$ containing NaCl (0.1 M) at room temperature under Ar atmosphere.

Table S1. Reduction potentials of $Na_2[Ni(pypzdt)_2]•6H_2O$ evaluated from the SWVs shown in Fig. S8. These values are employed to draw the Pourbaix diagrams depicted in Figs. 4 and S10.

pH	Reduction potential / V vs. SCE
8.24	-0.880
8.51	-0.904
8.87	-0.932
9.12	-0.956
9.57	-0.984
10.23	-1.032
10.42	-1.040
11.54	-1.112
11.96	-1.136
11.98	-1.136
12.19	-1.152
12.38	-1.160
12.42	-1.172
12.60	-1.172
12.68	-1.176
12.86	-1.180
12.96	-1.192
13.04	-1.192

Table S2. Oxidation potentials of $Na_2[Ni(pypzdt)_2]•6H_2O$ evaluated from the SWVs shown in Fig. S9. These values are employed to draw the Pourbaix diagrams depicted in Figs. 4 and S10.

pH	Oxidation potential / V vs. SCE
8.24	0.208
8.87	0.192
9.12	0.200
9.57	0.196
10.23	0.192
11.54	0.188
11.98	0.184
12.19	0.184
12.42	0.180
12.60	0.180
12.86	0.180

Table S3. Reduction potentials of $Na_2[Ni(qdt)_2]•6H_2O$ evaluated from the SWVs shown in Fig.S11. These values are employed to draw the Pourbaix diagram depicted in Fig. 4.

pH	Reduction potential / V vs. SCE
8.14	-0.940
9.09	-1.012
9.38	-1.032
9.66	-1.044
10.42	-1.096
11.82	-1.180
11.98	-1.192
12.28	-1.208
12.38	-1.212

Table S4. Oxidation potentials of $Na_2[Ni(qdt)_2]•6H_2O$ evaluated from the SWVs shown in Fig.S12. These values are employed to draw the Pourbaix diagram depicted in Fig. 4.

pH	Oxidation potential / V vs. SCE
8.14	0.176
9.09	0.180
9.38	0.172
9.66	0.176
10.42	0.176
11.82	0.176
12.28	0.168
12.38	0.180

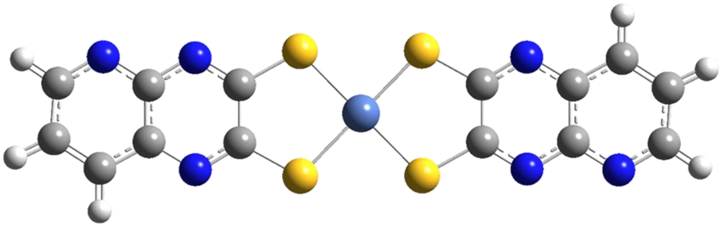
Table S5. Reduction potentials of $Na_2[Ni(dcpdt)_2]•4H_2O$ evaluated from the SWVs shown in Fig. S13. These values are employed to draw the Pourbaix diagram depicted in Fig. 4.

pH	Reduction potential / V vs. SCE
6.40	-1.088
6.57	-1.112
6.60	-1.136
6.69	-1.112
6.75	-1.128
6.80	-1.092
6.82	-1.136
6.83	-1.120
7.06	-1.148
7.19	-1.148
7.50	-1.188
7.59	-1.168
7.59	-1.176
7.67	-1.188
7.81	-1.184
7.95	-1.204
8.33	-1.224
8.41	-1.248
8.59	-1.236
8.77	-1.240
8.78	-1.256
8.90	-1.264
8.99	-1.268
9.00	-1.260
9.09	-1.272
9.16	-1.264
9.26	-1.264
9.40	-1.280
9.54	-1.272
9.62	-1.264

Table S6. Oxidation potentials of $Na_2[Ni(dcpdt)_2]•4H_2O$. These values are employed to draw the Pourbaix diagram depicted in Fig. 4.

pH	Oxidation potential / V vs. SCE
5.89	0.392
6.97	0.388
7.23	0.392
7.26	0.392
7.71	0.380
7.72	0.396
8.07	0.420

Table S7. Geometry optimized for $[Ni^{II}(pypzdt)_2]^{2-}$ in its singlet state. Optimized at the B3P86 level of DFT using the 6-311+G(d,p) basis set with solvation in water taken into consideration (C-PCM).



Atom	X	Y	Z
C1	-6.57416100	1.38321256	0.01455858
H1	-6.58480180	2.46778494	0.02533989
C2	-7.73279210	0.64042410	0.00752074
H2	-8.70715051	1.11365473	0.01250990
C3	-7.63411097	-0.76049557	-0.00624662
H3	-8.53925532	-1.36240236	-0.01168020
C4	7.63411277	0.76048651	-0.00650331
H4	8.53925654	1.36239015	-0.01207923
C5	7.73279237	-0.64043301	0.00734216
H5	8.70714712	-1.11366501	0.01225434
C6	6.57415926	-1.38321703	0.01454260
H6	6.58479810	-2.46779244	0.02538120
C7	-3.05304518	0.73669001	0.00796806
C8	-3.05844852	-0.71950550	-0.00858078
C9	-5.33896944	0.71458971	0.00765868
C10	-5.34681174	-0.70623563	-0.00694885
C11	3.05844887	0.71950862	-0.00836844
C12	3.05304366	-0.73668820	0.00817888
C13	5.34681280	0.70623225	-0.00694988
C14	5.33896896	-0.71459239	0.00772303
N1	-4.17932016	-1.40139827	-0.01488214
N2	-4.17258974	1.41785866	0.01485546

N3	-6.49061318	-1.42400121	-0.01342843
N4	4.17258756	-1.41785850	0.01502647
N5	4.17932245	1.40139759	-0.01477822
N6	6.49061540	1.42399429	-0.01359693
Ni1	-0.00000016	0.00000180	-0.00062828
S1	-1.54054375	-1.56566137	-0.02204408
S2	-1.53002896	1.57660277	0.02053762
S3	1.53002609	-1.57659841	0.02079234
S4	1.54054632	1.56566784	-0.02165316

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 Thermal correction to Enthalpy=                      0.209045
 Thermal correction to Gibbs Free Energy=           0.134920
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 Sum of electronic and thermal Free Energies=        -3971.564964

Item                    Value         Threshold   Converged?
 Maximum Force                  0.000009        0.000450         YES
 RMS          Force              0.000001        0.000300         YES
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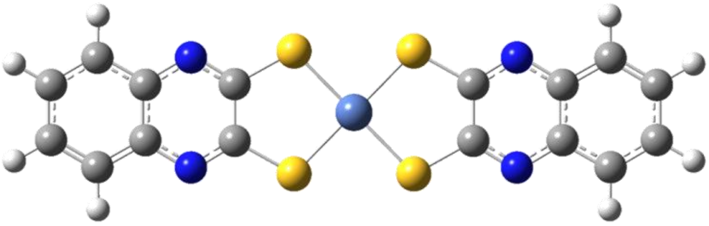
Table S8. Geometry optimized for $[Ni^{II}(qdt)_2]^{2-}$ in its singlet state. Optimized at the B3P86 level of DFT using the 6-311+G(d,p) basis set with solvation in water taken into consideration (C-PCM).



Atom	X	Y	Z
C1	6.58139210	-1.39988200	0.01922728
H1	6.56170645	-2.48441208	0.03408053
C2	7.77012513	-0.70408999	0.00957838
H2	8.71202000	-1.24128316	0.01692352
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C5	-7.77012572	0.70408793	0.00957045
H5	-8.71202090	1.24128064	0.01691521
C6	-6.58139306	1.39988058	0.01921497
H6	-6.56170793	2.48441069	0.03406460
C7	3.06107255	-0.72676783	0.01082253
C8	3.06107191	0.72677408	-0.01078653
C9	5.35211547	-0.70986011	0.00984137
C10	5.35211759	0.70985284	-0.00991980
C11	-3.06107187	-0.72677355	-0.01079542
C12	-3.06107327	0.72676798	0.01080925
C13	-5.35211748	-0.70985373	-0.00992670
C14	-5.35211616	0.70985930	0.00982976
N1	4.18033068	1.40840498	-0.01984587

N2	4.18033003	-1.40840060	0.01979858
N3	-4.18033099	1.40840040	0.01978334
N4	-4.18033018	-1.40840525	-0.01985177
Ni1	0.00000081	0.00000081	0.00006246
S1	1.53640089	1.57177599	-0.02710537
S2	1.53640215	-1.57176619	0.02721933
S3	-1.53640312	1.57176654	0.02720303
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C15	6.58137739	1.39987525	-0.01933080
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C16	-6.58137697	-1.39987683	-0.01933327
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Part of the Gaussian output file

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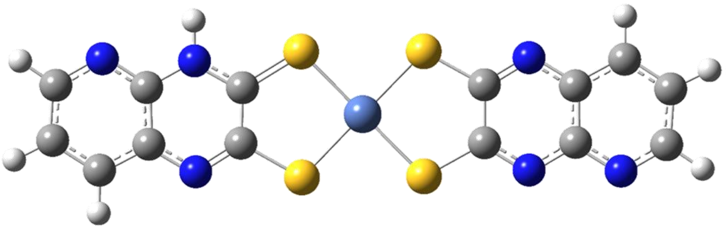
SCF Done:  E(RB3P86) =  -3939.59663620       A.U. after     19 cycles

                         1                       2                       3
                         A                       A                       A
 Frequencies --      15.2910                 32.9447                 38.2193
 Red. masses --       8.7858                  7.3656                 13.0461

Zero-point correction=                           0.210920 (Hartree/Particle)
 Thermal correction to Energy=                    0.231704
 Thermal correction to Enthalpy=                  0.232648
 Thermal correction to Gibbs Free Energy=         0.158796
 Sum of electronic and zero-point Energies=          -3939.399629
 Sum of electronic and thermal Energies=              -3939.378846
 Sum of electronic and thermal Enthalpies=            -3939.377902
 Sum of electronic and thermal Free Energies=         -3939.451754

         Item               Value     Threshold  Converged?
 Maximum Force            0.000010     0.000450     YES
 RMS     Force            0.000002     0.000300     YES
```

Table S9. Geometry optimized for [Ni(pypzdt)(pypzdtH^{-}•)]$^{2-}$ (most stable) in its doublet state. Optimized at UB3P86 level of DFT using the 6-311+G(d,p) basis set with solvation in water taken into consideration (C-PCM).



Atoms	X	Y	Z	Mulliken spin density
C1	-6.5823	-1.40483	-0.02484	0.108598
H2	-6.60031	-2.489	-0.04245	-0.009990
C3	-7.75841	-0.65836	-0.01322	-0.020173
H4	-8.72595	-1.14621	-0.02157	0.000562
C5	-7.67829	0.725058	0.009135	0.118139
H6	-8.57557	1.335684	0.01857	-0.008829
C7	7.664958	-0.76653	0.007269	0.002842
H8	8.568863	-1.37026	0.014847	-0.000239
C9	7.765841	0.6335	-0.01374	0.000694
H10	8.740839	1.105449	-0.02206	-0.000058
C11	6.607777	1.378214	-0.02365	0.002360
H12	6.620368	2.462729	-0.04016	-0.000245
C13	-3.02982	-0.72864	-0.01275	-0.028400
C14	-2.99118	0.664799	0.012347	0.313260
C15	-5.34283	-0.75396	-0.01374	-0.081991
C16	-5.39817	0.671021	0.009473	0.050953
C17	3.088342	-0.718	0.014304	-0.001046
C18	3.085185	0.738114	-0.01165	-0.000781
C19	5.377175	-0.7088	0.010076	0.000333
C20	5.371616	0.712193	-0.01226	-0.000695
N21	-4.19683	1.337445	0.021521	0.140813
N22	-4.16538	-1.44617	-0.02525	0.294487
N23	-6.51034	1.391194	0.020561	0.021191
N24	4.206169	1.417735	-0.02283	0.007540
N25	4.208278	-1.40214	0.02331	0.006073
N26	6.519676	-1.42808	0.019059	0.000869

Ni27	0.027875	-0.00033	0.00162	-0.007391
S28	-1.51751	1.570524	0.033258	0.085134
S29	-1.49612	-1.58837	-0.03074	0.030543
S30	1.562952	1.577182	-0.0319	-0.011901
S31	1.569254	-1.56119	0.037735	-0.003168
H32	-4.21638	2.348049	0.038698	-0.009485

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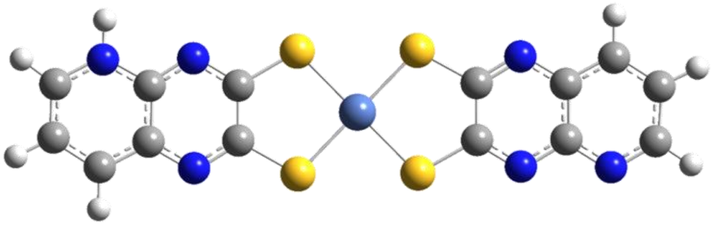
```
SCF Done:    E(UB3P86) =    -3972.29526724         A.U. after      32 cycles

                          1                          2                          3
                          A                          A                          A
 Frequencies --      13.8682                    35.5827                    41.1002
 Red. masses --       9.3892                     8.6823                    11.8829

Zero-point correction=                           0.198328 (Hartree/Particle)
 Thermal correction to Energy=                    0.219425
 Thermal correction to Enthalpy=                  0.220369
 Thermal correction to Gibbs Free Energy=         0.145270
 Sum of electronic and zero-point Energies=        -3972.103562
 Sum of electronic and thermal Energies=            -3972.082464
 Sum of electronic and thermal Enthalpies=          -3972.081520
 Sum of electronic and thermal Free Energies=      -3972.156619

          Item                 Value        Threshold    Converged?
 Maximum Force                0.000002       0.000450        YES
 RMS          Force            0.000001       0.000300        YES
```

Table S10. Geometry optimized for [Ni(pypzdt)(pypzdtH^{-}•)]$^{2-}$ (+0.54 kcal/mol) in its doublet state. Optimized at UB3P86 level of DFT using the 6-311+G(d,p) basis set with solvation in water taken into consideration (C-PCM).



Atoms	X	Y	Z	Mulliken spin density
C1	6.571017	-1.4103	0.022791	0.374688
H2	6.596801	-2.49317	0.039838	-0.026901
C3	7.756238	-0.65395	0.011068	-0.093804
H4	8.722248	-1.1426	0.018943	0.003596
C5	7.70745	0.712366	-0.01021	0.279976
H6	8.576458	1.353432	-0.01993	-0.018943
C7	-7.67678	-0.74893	-0.01058	0.002454
H8	-8.58289	-1.34937	-0.01927	-0.000209
C9	-7.77241	0.651302	0.010811	0.000700
H10	-8.7456	1.127015	0.018381	-0.000057
C11	-6.61132	1.39161	0.02202	0.002182
H12	-6.61989	2.476183	0.038834	-0.000222
C13	3.019128	-0.7313	0.012922	0.032774
C14	3.017793	0.677337	-0.01248	0.180756
C15	5.319738	-0.75952	0.01256	-0.117077
C16	5.291236	0.66996	-0.0105	0.020981
C17	-3.09893	-0.7182	-0.01329	-0.000382
C18	-3.09043	0.738837	0.01274	-0.000784
C19	-5.38848	-0.69987	-0.01112	0.000018
C20	-5.37766	0.721129	0.011514	-0.000461
N21	4.174509	1.374509	-0.023	0.032967
N22	4.153397	-1.43921	0.024191	0.137302
N23	6.487828	1.343684	-0.02049	0.116229
N24	-4.20954	1.422221	0.023168	0.006628
N25	-4.2223	-1.39763	-0.02333	0.005536
N26	-6.53379	-1.41474	-0.02145	0.000907

Ni27	-0.03388	-0.00615	-0.0004	0.000078
S28	1.510464	1.556272	-0.03299	0.056539
S29	1.489579	-1.58975	0.032305	0.023293
S30	-1.56589	1.573941	0.033634	-0.007945
S31	-1.58344	-1.56655	-0.03496	-0.003971
H32	6.439633	2.353151	-0.03653	-0.006847

Part of the Gaussian output file

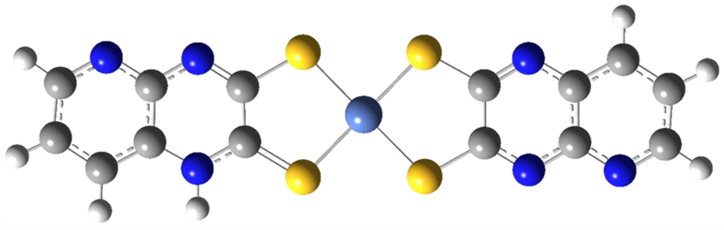
```
SCF Done:   E(UB3P86) =   -3972.29600309        A.U. after      32 cycles

                          1                          2                          3
                          A                          A                          A
 Frequencies --     13.8151                     36.5473                     42.6298
 Red. masses --       9.2636                      7.9301                     12.1563

Zero-point correction=                              0.198232 (Hartree/Particle)
 Thermal correction to Energy=                       0.219234
 Thermal correction to Enthalpy=                     0.220179
 Thermal correction to Gibbs Free Energy=           0.145386
 Sum of electronic and zero-point Energies=          -3972.102906
 Sum of electronic and thermal Energies=               -3972.081904
 Sum of electronic and thermal Enthalpies=            -3972.080960
 Sum of electronic and thermal Free Energies=        -3972.155752

           Item                   Value       Threshold   Converged?
 Maximum Force                  0.000002       0.000450        YES
 RMS         Force               0.000000       0.000300        YES
```

Table S11. Geometry optimized for [Ni(pypzdt)(pypzdtH^{-}•)]$^{2-}$ (+1.23 kcal/mol) in its doublet state. Optimized at UB3P86 level of DFT using the 6-311+G(d,p) basis set with solvation in water taken into consideration (C-PCM).



Atoms	X	Y	Z	Mulliken spin density
C1	-6.61182	1.349782	0.018466	0.052247
H2	-6.64995	2.434153	0.03584	-0.005534
C3	-7.77763	0.583711	0.0049	0.070939
H4	-8.75348	1.053222	0.011456	-0.004750
C5	-7.6582	-0.79769	-0.01704	0.027727
H6	-8.5486	-1.42089	-0.02778	-0.003408
C7	7.667534	0.752002	-0.01736	0.002422
H8	8.573544	1.352529	-0.0279	-0.000216
C9	7.763549	-0.64841	0.003713	0.001243
H10	8.736915	-1.12375	0.009128	-0.000090
C11	6.602937	-1.38905	0.017332	0.001968
H12	6.611771	-2.47359	0.034	-0.000226
C13	-2.98528	0.686845	0.012949	0.311640
C14	-3.03373	-0.7052	-0.0122	-0.005064
C15	-5.39022	0.694677	0.009145	0.029286
C16	-5.34979	-0.73326	-0.01411	-0.062837
C17	3.090753	0.719813	-0.01128	-0.000287
C18	3.082752	-0.73622	0.015015	-0.000809
C19	5.379574	0.702311	-0.01321	-0.000524
C20	5.369116	-0.71864	0.009531	0.000249
N21	-4.17468	-1.41752	-0.02513	0.271672
N22	-4.18509	1.362702	0.022324	0.157162
N23	-6.48977	-1.44748	-0.02653	0.078641
N24	4.201122	-1.4199	0.023528	0.007120
N25	4.21322	1.39992	-0.02322	0.006870
N26	6.524608	1.417563	-0.02586	0.001254

Ni27	0.028246	-0.00041	0.00282	-0.012389
S28	-1.50824	-1.5761	-0.03071	0.034011
S29	-1.50554	1.582295	0.034698	0.067409
S30	1.558224	-1.57275	0.03937	-0.004293
S31	1.573943	1.565684	-0.03107	-0.011251
H32	-4.1785	2.372715	0.038736	-0.010184

Part of the Gaussian output file

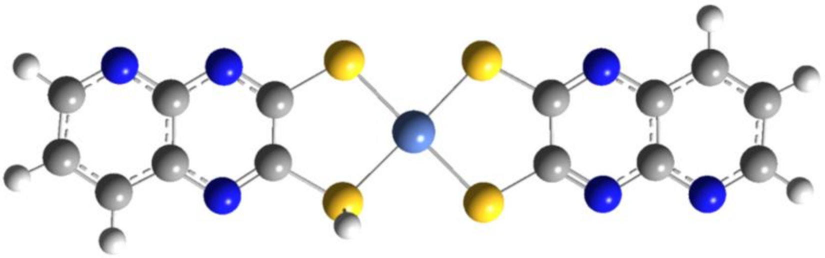
```
SCF Done:   E(UB3P86) =   -3972.29273676        A.U. after     30 cycles

                            1                          2                          3
                            A                          A                          A
 Frequencies --       10.6846                    35.8187                    39.7458
 Red. masses --        9.2580                     8.5773                    11.5089

Zero-point correction=                            0.198232 (Hartree/Particle)
 Thermal correction to Energy=                     0.219419
 Thermal correction to Enthalpy=                   0.220363
 Thermal correction to Gibbs Free Energy=          0.144787
 Sum of electronic and zero-point Energies=        -3972.101208
 Sum of electronic and thermal Energies=           -3972.080021
 Sum of electronic and thermal Enthalpies=         -3972.079077
 Sum of electronic and thermal Free Energies=      -3972.154653

           Item               Value     Threshold  Converged?
 Maximum Force            0.000004     0.000450     YES
 RMS     Force            0.000001     0.000300     YES
```

Table S12. Geometry optimized for $[\mathrm{Ni(pypzdt)(pypzdtH^{-}\bullet)}]^{2-}$ (+25.9 kcal/mol) in its doublet state. Optimized at UB3P86 level of DFT using the 6-311+G(d,p) basis set with solvation in water taken into consideration (C-PCM).



Atoms	X	Y	Z	Mulliken spin density
C1	6.606372	1.345455	0.159279	-0.000046
H2	6.639728	2.429804	0.179495	0.000282
C3	7.766556	0.576932	0.209821	-0.000020
H4	8.744032	1.041769	0.272455	0.000246
C5	7.650969	-0.80489	0.178206	-0.000054
H6	8.539723	-1.42974	0.215481	0.096395
C7	-7.65142	0.724373	0.161505	0.042523
H8	-8.56107	1.318312	0.196614	-0.061968
C9	-7.73792	-0.67783	0.16949	-0.014406
H10	-8.70748	-1.15906	0.210253	-0.001062
C11	-6.57454	-1.41096	0.125427	-0.000110
H12	-6.57576	-2.49556	0.129627	0.000855
C13	3.082856	0.69398	-0.03834	-0.000739
C14	3.046174	-0.69478	-0.05687	0.222963
C15	5.358726	0.708296	0.079315	0.327372
C16	5.345487	-0.73445	0.054614	0.051640
C17	-3.08225	0.721366	-0.02381	0.001539
C18	-3.064	-0.73199	-0.01665	0.001634
C19	-5.36645	0.689267	0.068855	0.000377
C20	-5.34616	-0.73133	0.073511	-0.007796
N21	4.171334	-1.42459	-0.01724	0.010967
N22	4.206847	1.429875	0.021995	0.029470
N23	6.478017	-1.45506	0.102653	-0.002719
N24	-4.17446	-1.42432	0.029968	0.001337
N25	-4.20584	1.394865	0.017889	0.030268
N26	-6.51506	1.397558	0.113461	-0.000046

Ni27	-0.02395	0.013391	-0.11527	0.000282
S28	1.512757	-1.56833	-0.11855	-0.000020
S29	1.542442	1.573482	-0.19989	0.000246
S30	-1.53367	-1.56046	-0.06942	-0.000054
S31	-1.57062	1.577775	-0.09814	0.096395
H32	1.444362	2.091116	1.05241	0.042523

Part of the Gaussian output file

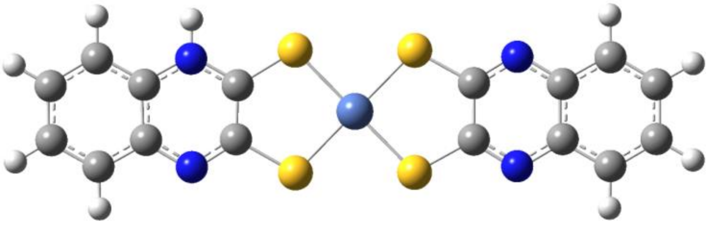
```
SCF Done:   E(UB3P86) =   -3972.24570846        A.U. after     39 cycles

                          1                          2                          3
                           A                          A                          A
 Frequencies --      16.8253                    26.4924                    36.0896
 Red. masses --        9.1122                    10.9581                    11.4153

Zero-point correction=                           0.194199 (Hartree/Particle)
 Thermal correction to Energy=                    0.215369
 Thermal correction to Enthalpy=                  0.216313
 Thermal correction to Gibbs Free Energy=         0.140842
 Sum of electronic and zero-point Energies=         -3972.061973
 Sum of electronic and thermal Energies=              -3972.040803
 Sum of electronic and thermal Enthalpies=           -3972.039859
 Sum of electronic and thermal Free Energies=        -3972.115330

           Item                  Value      Threshold   Converged?
 Maximum Force              0.000005     0.000450       YES
 RMS         Force              0.000001     0.000300       YES
```

Table S13. Geometry optimized for [Ni(qdt)(qdtH^{-}•)]$^{2-}$ in its doublet state. Optimized at UB3P86 level of DFT using the 6-311+G(d,p) basis set with solvation in water taken into consideration (C-PCM).



Atoms	X	Y	Z	Mulliken spin density
C1	6.610969	-1.40454	0.023123	0.000433
H2	6.589651	-2.48899	0.042939	-0.000082
C3	7.801327	-0.71081	0.008852	0.001360
H4	8.742239	-1.24974	0.017485	-0.000102
C5	7.803535	0.696882	-0.01678	0.000791
H6	8.74612	1.232843	-0.02768	-0.000068
C7	-7.79393	-0.7403	-0.01703	-0.013506
H8	-8.72367	-1.29857	-0.02838	-0.000144
C9	-7.81634	0.653312	0.00991	0.083150
H10	-8.75925	1.187967	0.019833	-0.005671
C11	-6.61968	1.365372	0.024334	0.002412
H12	-6.62424	2.450875	0.04517	-0.001639
C13	3.09139	-0.72617	0.016132	-0.001323
C14	3.093593	0.727419	-0.01374	-0.001061
C15	5.382846	-0.71296	0.012098	0.000932
C16	5.385063	0.706673	-0.01439	0.000049
C17	-3.03804	-0.7157	-0.01432	-0.030920
C18	-2.99386	0.674564	0.014367	0.326782
C19	-5.35519	-0.73359	-0.01555	-0.105306
C20	-5.40288	0.687254	0.011696	0.109917
N21	4.214202	1.407473	-0.02688	0.005958
N22	4.209661	-1.40988	0.027087	0.005223
N23	-4.19401	1.356667	0.025898	0.168895
N24	-4.17471	-1.43298	-0.02901	0.324545
Ni25	0.028338	-0.00101	0.001618	-0.011493
S26	1.569756	1.571704	-0.03663	-0.010571

S27	1.565482	-1.56832	0.042166	-0.002391
S28	-1.51266	1.575821	0.03768	0.070418
S29	-1.5041	-1.58249	-0.03487	0.025279
C30	6.61536	1.394361	-0.02826	0.000995
H31	6.597396	2.478879	-0.04811	-0.000112
C32	-6.58204	-1.41907	-0.02955	0.074822
H33	-6.552	-2.50338	-0.05046	-0.006271
H34	-4.18421	2.365748	0.045095	-0.011303

Part of the Gaussian output file

```
SCF Done:  E(UB3P86) =  -3940.19598275     A.U. after    33 cycles

                        1                          2                          3
                        A                          A                          A
 Frequencies --    14.6835                    38.4769                    42.4723
 Red. masses --      8.6438                     6.6786                    10.6216

Zero-point correction=                           0.221381 (Hartree/Particle)
 Thermal correction to Energy=                    0.242921
 Thermal correction to Enthalpy=                  0.243865
 Thermal correction to Gibbs Free Energy=         0.168262
 Sum of electronic and zero-point Energies=       -3939.985746
 Sum of electronic and thermal Energies=          -3939.964206
 Sum of electronic and thermal Enthalpies=        -3939.963262
 Sum of electronic and thermal Free Energies=     -3940.038865

          Item               Value     Threshold  Converged?
 Maximum Force            0.000002     0.000450     YES
 RMS     Force            0.000000     0.000300     YES
```

Table S14. A) Elemental analysis for the precipitate which was afforded after mixing an aqueous phosphate buffer solution (0.1 M; pH = 7.0) with the same volume of an aqueous solution of $Na_2[Ni(pypzdt)_2]•6H_2O$. B) Elemental analysis for the precipitate which was afforded after mixing an aqueous acetate buffer solution (0.1 M; pH = 5.0) with the same volume of an aqueous solution of $Na_2[Ni(qdt)_2]•6H_2O$.

A)

Element	H (%)	C (%)	N (%)
Found	2.11	35.42	17.60
Calcd. for $Ni(pypzdtH)_2•1.5H_2O$ (i.e., $C_{14}H_8N_6NiS_4•1.5H_2O$)	2.34	35.46	17.72
Δ	0.23	0.04	0.12

B)

Element	H (%)	C (%)	N (%)
Found	2.89	39.19	11.52
Calcd. for $Ni(qdtH)_2•2.5H_2O$ ($C_{16}H_{10}N_4NiS_4•2.5H_2O$)	3.08	39.20	11.43
Δ	0.19	0.01	0.09

Determination of the turnover frequencies (TOF's)

The TOF in the electrochemical hydrogen evolution reaction (HER) can be determined by using the following eq. 1,[13,14]

$$k_{obs} = \frac{1}{D_{cat}}\left(\frac{i_c}{nFA[cat]}\right)^2 \qquad (1)$$

where D_{cat} is the diffusion coefficient of the catalyst, i_c is the maximum current at the catalytic peak, n is the number of electrons (2 electrons), F is the Faraday constant (9.6485×10^4 [C mol^{-1}]), A is the surface area of the electrode ($0.15^2 \times 3.14 = 7.07 \times 10^{-2}$ [cm^2]), and [*cat*] is the concentration of the catalyst in solution (5.0×10^{-7} [mol cm^{-3}])). $D_{[Ni(pypzdt)_2]^{2-}}$, and $D_{[Ni(qdt)_2]^{2-}}$ were estimated as 4.1×10^{-6} [cm^2 s^{-1}] (see below) and 2.8×10^{-6} [cm^2 s^{-1}],[15] respectively. Thus, the k_{obs}'s (i.e., TOF$_{max}$'s) of $[Ni^{II}(pypzdt)_2]^{2-}$ and $[Ni^{II}(qdt)_2]^{2-}$ were calculated as TOF$_{max}$ = 3.5 and 3.2 s^{-1}, respectively.

Estimation of the diffusion coefficients (*D'*s)

The D value of $[Ni^{II}(pypzdt)_2]^{2-}$ was estimated in the same manner as described for $[Ni^{II}(qdt)_2]^{2-}$ and $[Ni^{II}(dcpdt)_2]^{2-}$.[15] This is due to the problem of its adsorption onto the glassy carbon electrode surfaces only upon the anodic polarization performed for its aqueous solutions, even though the adsorption was found to be negligible upon the polarization using its DMF solutions. Because of the problem, we had to indirectly estimate the $D(H_2O)$ value of $[Ni^{II}(pypzdt)_2]^{2-}$ using the observable D(DMF) value, as explained below. In our approach, the $D^{\frac{2}{3}}\nu^{-\frac{1}{6}}$ values, i.e., x_{obs} values defined in eq. 2 (see below), were measured for the relevant systems including the reference compound (i.e., Methylene Blue). The measurements were carried out using the BAS RRDE-3A rotating ring disk electrode system and a glassy carbon disk electrode (5 mmφ, 0.196 cm^2). The x_{obs} values measured are defined by the so-call Levich equation, eq. 2,[16]

$$i = 0.62nFACD^{\frac{2}{3}}\upsilon^{-\frac{1}{6}}\omega^{\frac{1}{2}} \qquad (2)$$

$$= 0.62nFACx_{obs}\omega^{\frac{1}{2}}$$

where i is the limiting current, n is the number of electron (1 electron), A is the surface area of the electrode (0.25^2 × 3.14 = 0.196 [cm^2]), C is the concentration of the electroactive species (5.0 × 10^{-7} [mol cm^{-3}]), ν is the kinematic viscosity [cm^2 s^{-1}], and ω is the angular rotation rate of the electrode [rad s^{-1}]. One can understand that *D* is a solvent-independent value, while x_{obs} is dependent on the choice of solvent. Therefore, the $x_{obs}(H_2O)$ value can be estimated by adopting the observed $x_{obs}(DMF)$ value using the following equation (eq. 3).

$$x_{calcd}(H_2O) = x_{obs}(DMF) \times \left(\nu_{H_2O}/\nu_{DMF}\right)^{-1/6} \qquad (3)$$

The validity of this approach has also been confirmed, and the *D* value for $[\mathrm{Ni^{II}(pypzdt)_2}]^{2-}$ could also be benchmarked using the literature value of *D* reported for Methylene Blue (see Table S15), as described elsewhere.[15]

Table S15. Diffusion coefficients (*D*'s) of $[\mathrm{Ni^{II}(pypzdt)_2}]^{2-}$ and Methylene Blue.

Compounds	$\chi_{obs}(H_2O)$ [a]	$\chi_{calcd}(H_2O)$	$\chi_{obs}(DMF)$ [b]	$(\nu_{H2O}/\nu_{DMF})^{-1/6}$	D_{calcd} [$cm^2\ s^{-1}$]	D_{ref} [$cm^2\ s^{-1}$]	ref
$[\mathrm{Ni^{II}(pypzdt)_2}]^{2-}$	– [c]	2.8×10^{-4} [d]	2.8×10^{-4}	0.99 [e]	4.1×10^{-6} [f]	–	–
Methylene Blue	3.8×10^{-4}	–	3.6×10^{-4}	1.03	6.3×10^{-6} [g]	6.3×10^{-6} [g]	17

[a] Determined in an aqueous solution.

[b] Determined in DMF solutions.

[c] The value not determined directly due to the adsorption of the compound over the electrode surfaces upon the anodic polarization.

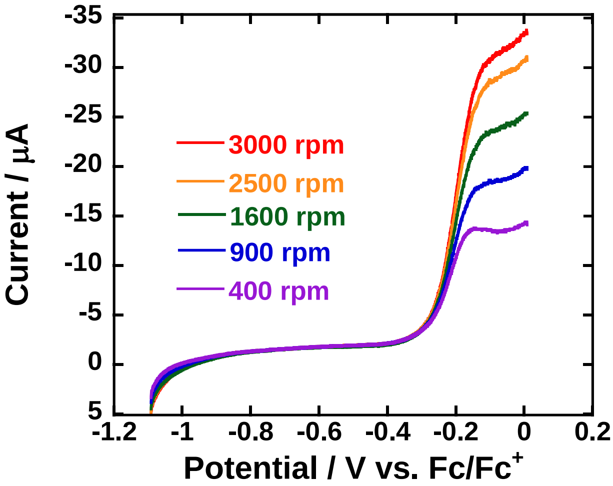
[d] $\chi_{calcd}(H_2O, [Ni(pypzdt)_2]^{2-}) = \chi_{obs}(DMF, [Ni(pypzdt)_2]^{2-}) \times \left(v_{H_2O}/v_{DMF}\right)^{-1/6}$

[e] Calculated from the reported values.[18,19]

[f] $D_{calcd}([Ni(pypzdt)_2]^{2-}) = D_{ref}(MB) \times \{\chi_{calcd}(H_2O, [Ni(pypzdt)_2]^{2-})/\chi_{obs}(H_2O, MB)\}^{3/2}$

[g] Used as the benchmark. $D_{calcd}(MB) = D_{ref}(MB) \times \{x_{obs}(H_2O, MB)/x_{obs}(H_2O, MB)\}^{3/2}$

A)



B)

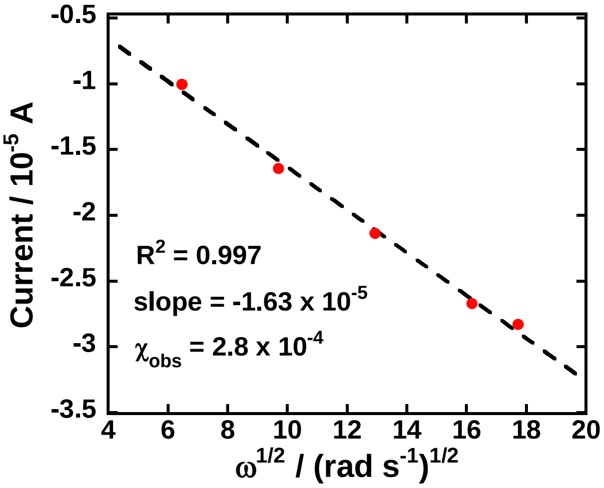


Fig. S14 (A) LSVs of 0.5 mM $[Ni(pypzdt)_2]^{2-}$ in DMF containing 0.1 M $TBAPF_6$ recorded by using a rotating ring disk electrode apparatus (*ω* = 400-3000 rpm), at a sweep rate of 100 mV/s, under Ar atmosphere at room temperature. (B) The plots of its limiting current versus $\omega^{1/2}$.

Table S16. The $\eta(E_{\mathrm{cat/2}})$ values for HER catalyzed by $[\mathrm{Ni(pypzdt)_2}]^{2-}$ and $[\mathrm{Ni(qdt)_2}]^{2-}$ at pH = 9.0, where $E_{1/2}$ $(2\mathrm{H^+/H_2})$ = -0.772 V vs. SCE.

	$[\mathrm{Ni(pypzdt)_2}]^{2-}$	$[\mathrm{Ni(qdt)_2}]^{2-}$
$E_{\mathrm{cat/2}}$ / V vs. SCE	-0.945	-0.999
$\eta(E_{\mathrm{cat/2}})$ / V	0.173	0.227

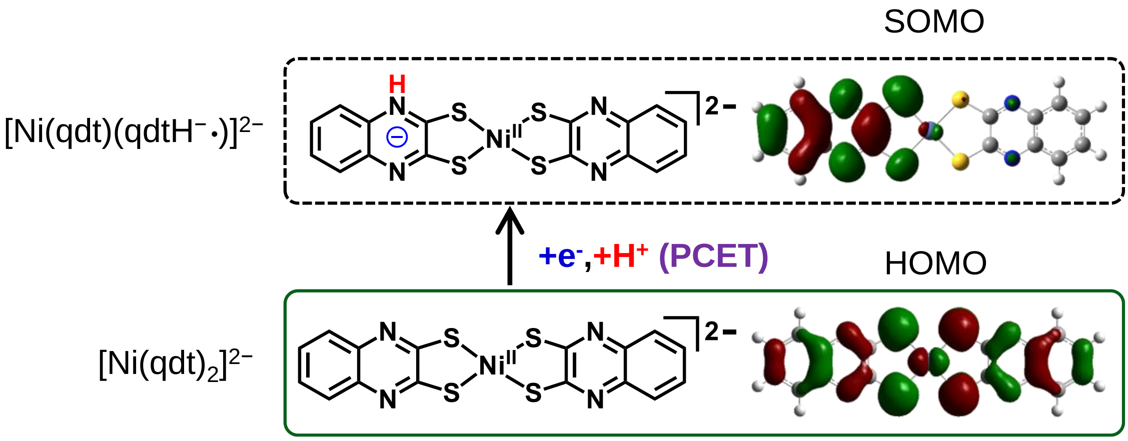


Fig. S15 The geometries and molecular orbitals relevant to the PCET-based reduction processes of $[\mathrm{Ni(qdt)_2}]^{2-}$, optimized at the UB3P86/6-311+G(d,p) level of DFT with solvation in water taken into consideration (C-PCM).

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