Supporting Information

Consecutive Ligand-based PCET Processes Affording a Doubly Reduced Nickel Pyrazinedithiolate which Transforms into a Metal Hydride Required to Evolve H_2.

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Computational Method

Density functional theory (DFT) calculations were performed using Gaussian 09/16 packages[1] to understand the structural and spin-state candidates. The structures were fully optimized using the B3P86 density functuonal[2,3] with the effect of solvation in water taken into consideration using the conductor-like polarizable continuum model (C-PCM) method.[4,5] The 6-311+G(2d,p) basis set was applied to all atoms. The use of B3P86/6-311+G(2d,p) level of DFT was reported to show good consistency with theoretical and experimental results for the 1st row transition metal complexes,[6-9] which were further confirmed by our calculations on model systems (data not shown). The redox potentials and pK_a values are calculated as described in Scheme S1. The structure of the transition state was determined using the TS and QST3 methods, followed by performing the intrinsic reaction coordinate (IRC) calculations.

Scheme S1. Isodesminc reaction methods[6-14] for calculating redox potentials and pK_a values based on the experimentally determined values for the oxidation potential of $[Ni^{II}(dcpdt)_2]^{2-}$ (+0.39 V vs. SCE; dcpdt = 5,6-dicyanopyrazine-2,3-dithiolate) and pK_a for $[Ni^{II}(dcpdt)(dcpdtH)]^-$ (pK_a = 5.0), respectively. F is Faraday constant, R is the gas constant, and T is temperature (298.15 K).

(1) Determination of the redox potential for $Ox + e^- \rightarrow Red$

$Ox + e^- \rightarrow Red \qquad \Delta G^0 = -FE^0$

$[Ni^{II}(dcpdt)_2]^{2-} \rightarrow [Ni^{II}(dcpdt)(dcpdt^+\bullet)]^- + e^-$

$\Delta G^0_{ref} = -FE^0_{ref} \qquad E^0_{ref} = 0.39$ V vs. SCE

$Ox + [Ni^{II}(dcpdt)_2]^{2-} \rightarrow Red + [Ni^{II}(dcpdt)(dcpdt^+\bullet)]^-$

$\Delta G^0_r = G(Red)_{solv} + G([Ni^{II}(dcpdt)(dcpdt^+\bullet)]^-)_{solv} - G(Ox)_{solv} - G([Ni^{II}(dcpdt)_2]^{2-})_{solv}$

$\Delta G^0_r = -\Delta G^0_{ref} + \Delta G^0 = FE^0_{ref} - FE^0$

$E^0 = -\Delta G^0_r/F + E^0_{ref}$

(2) Determination of pK_a value for $A + H^+ \rightarrow AH^+$

$A + H^+ \rightarrow AH^+ \qquad \Delta G^0 = RT\ln(10)pK_a$

$[Ni^{II}(dcpdt)_2]^{2-} + H^+ \rightarrow [Ni(dcpdt)(dcpdtH)]^-$

$\Delta G^0_{ref} = RT\ln(10)pK_{a,ref} \quad pK_{a,ref} = 5.0$

$A + [Ni^{II}(dcpdt)(dcpdtH)]^- \rightarrow AH^+ + [Ni^{II}(dcpdt)_2]^{2-}$

$\Delta G^0_r = G(AH^+)_{solv} + G([Ni^{II}(dcpdt)_2]^{2-})_{solv} - G(A)_{solv} - G([Ni^{II}(dcpdt)(dcpdtH)]^-)_{solv}$

$\Delta G^0_r = RT\ln(10)pK_a - RT\ln(10)pK_{a,ref}$

$pK_a = \Delta G^0_r/RT\ln(10) + pK_{a,ref}$

Scheme S2. Free energy changes relevant to the catalytic processes by $[Ni^{II}(dcpdt)_2]^{2-}$ (**M**$^{2-}$) at each pH condition, as reported elsewhere.[15]

$2H^+ + 2e^- \rightarrow H_2$ $\quad E^0_{2H^+/H2} = -0.241 - 0.0592 \times pH$ (V vs. SCE)

$\Delta G_{2H^+/H2} = -2F(E^0_{2H^+/H2} - E)$

$\mathbf{MH}^- + e^- \rightarrow \mathbf{MH}^{2-}$ $\quad E^0_{\mathbf{MH}^-/\mathbf{MH}^{2-},cal} = -0.707$ (V vs. SCE)

$\Delta G_{\mathbf{MH}^+/\mathbf{MH}} = -F(E^0_{\mathbf{MH}^-/\mathbf{MH}^{2-},cal} - E)$

$\mathbf{MH}^{2-} + H^+ \rightarrow \mathbf{MH_2}^-$ $\quad pK_{a,\mathbf{MH}^{2-}/\mathbf{MH2}^-,cal} = 13.0$

$\Delta G_{\mathbf{MH/MH2}^+} = -RT\ln(10) \times (pK_{a,\mathbf{MH}^{2-}/\mathbf{MH2}^-,cal} - pH)$

$\mathbf{MH_2}^- + e^- \rightarrow \mathbf{MH_2}^{2-}$ $\quad E^0_{\mathbf{MH2}^-/\mathbf{MH2}^{2-},cal} = -0.786$ (V vs. SCE)

$\Delta G_{\mathbf{MH2}^+/\mathbf{MH2}} = -F(E^0_{\mathbf{MH2}^-/\mathbf{MH2}^{2-},cal} - E)$

$\mathbf{MH_2}^{2-} + H^+ \rightarrow \mathbf{MH_3}^-$ $\quad pK_{a,\mathbf{MH2}^{2-}/\mathbf{MH3}^-,cal} = 7.21$

$\Delta G_{\mathbf{MH2/MH3}^+} = -RT\ln(10) \times (pK_{a,\mathbf{MH2}^{2-}/\mathbf{MH3}^-,cal} - pH)$

$\mathbf{MH_3}^- \rightarrow \mathbf{MH_3}^-$(hydride)

$\Delta G_{\mathbf{MH3}^-/\mathbf{MH3}^-}$(hydride) = 12.3 kcal/mol

$\mathbf{MH_3}^-$(hydride) $\rightarrow \mathbf{MH}^- + H_2$

$\Delta G_{\mathbf{MH3}^-\text{(hydride)}/\mathbf{MH}^-+H2} = \Delta G_{2H^+/H2} - \Delta G_{\mathbf{MH}^-/\mathbf{MH}^{2-}} - \Delta G_{\mathbf{MH}^{2-}/\mathbf{MH2}^-} - \Delta G_{\mathbf{MH2}^-/\mathbf{MH2}^{2-}}$
$- \Delta G_{\mathbf{MH2}^{2-}/\mathbf{MH3}^-} - \Delta G_{\mathbf{MH3}^-/\mathbf{MH3}^-\text{(hydride)}}$

Measurements

Linear sweep voltammetry was performed on a BAS ALS 602DKM electrochemical analyzer and a BAS RRDE-3A Rotating Ring Disk Electrode Apparatus. For the experiments for the aqueous solutions, a glassy carbon working electrode (5 mmϕ), a platinum wire counter electrode and a saturated calomel reference electrode (SCE; 0.241 V *vs.* NHE) were employed, where NaCl (0.1 M) was used as a supporting electrolyte. For the experiments for the organic solutions, a glassy carbon 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 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 plate 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.[16] The pH measurements were performed using a DKK-TOA HM-25R pH meter.

Materials

All solvents and reagents were of the highest qualities available and were used as received without further purification. $Na_2[Ni^{II}(dcpdt)_2]\bullet 4H_2O$ (dcpdt = 5,6-dicyanopyrazine-2,3-dithiolate)[17] and $Na_2[Ni^{II}(qdt)_2]\bullet 6H_2O$ (qdt = quinoxline-2,3-dithiolate)[18] were synthesized as previously described. The compounds 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride (Methylene Blue; Shuzui-Hikotaro Co., Ltd.), and potassium hexacyanoferrate(III) ($K_3[Fe^{III}(CN)_6]$; Kanto Chemical Co., Inc.) were used as received.

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,[19-20]

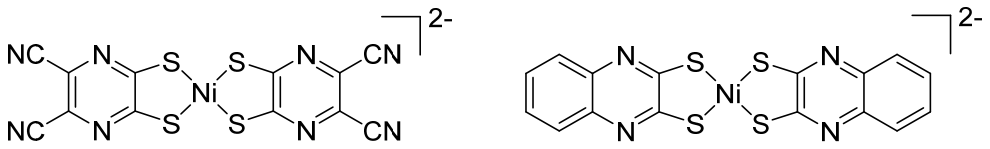
$$k_{obs} = \frac{1}{D_{[Ni(dcpdt)_2]^{2-}}}\left(\frac{i_c}{nFA[cat]}\right)^2 \qquad (1)$$

where $D_{[Ni(dcpdt)_2]^{2-}}$ is the diffusion coefficient of $[Ni^{II}(dcpdt)_2]^{2-}$ (aproximately obtained 2.8×10^{-6} [cm^2 s^{-1}]; see below), 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 $[Ni^{II}(dcpdt)_2]^{2-}$ in solution (5.0×10^{-7} [mol cm^{-3}])). The k_{obs} (i.e., TOF_{max}) were calculated as TOF_{max} = 11.7, 6.7 and 2.1 s^{-1} at pH = 4, 5 and 6, respectively.

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

Our attempts to determine the diffusion coefficient (*D*) of $[Ni(dcpdt)_2]^{2-}$ failed due to the strong adsorption of the catalyst over the electrode surfaces while its polarization under all conditions examined, regardless of the choice of solvent, such as water, acetonitrile, DMF and so on. Because of such problematic situation, we decided to adopt the *D* value estimated for $[Ni^{II}(qdt)_2]^{2-}$ as a *D* value approximated for $[Ni(dcpdt)_2]^{2-}$. We think this is a reasonable approach because of the good resemblance of the two catalysts from the viewpoints of both the molecular size and the dianionic

nature of the systems, as depicted in the following structure diagrams (Scheme S3).



Scheme S3. The structures of $[Ni^{II}(dcpdt)_2]^{2-}$ (left) and $[Ni^{II}(qdt)_2]^{2-}$ (right).

In the determination of the *D* value of $[Ni^{II}(qdt)_2]^{2-}$, an additional problem arose due to 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 these multiple problems, we had to indirectly estimate the $D(H_2O)$ value of $[Ni^{II}(qdt)_2]^{2-}$ 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 compounds (i.e., Methylene Blue and $[Fe^{III}(CN)_6]^{3-}$). The measurements were carried out using the BAS RRDE-3A Rotating Ring Disk Electrode systems 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,[21]

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

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

where i is the limiting current, n is the number of electron (1 electron), A is the surface area of the electrode ($0.25^2 \times 3.14 = 0.196$ [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 by measuring the x_{obs} values of $[Fe^{III}(CN)_6]^{3-}$ and Methylene Blue. Moreover, the *D* values for the Ni compounds could also be benchmarked using the literature values of *D*'s reported for these reference compounds, as summarized in Table S1.

Table S1. Diffusion coefficients (D's) of $[Ni^{II}(dcpdt)_2]^{2-}$, $[Ni^{II}(qdt)_2]^{2-}$, $[Fe^{III}(CN)_6]^{3-}$ and Methylene Blue.

Compounds	$x_{obs}(H_2O)$ [a]	$x_{calcd}(H_2O)$	$x_{obs}(DMF)$ [b]	$\left(\nu_{H_2O}/\nu_{DMF}\right)^{-1/6}$	D_{calcd} [$cm^2\ s^{-1}$]	D_{ref} [$cm^2\ s^{-1}$]	ref
$[Ni^{II}(dcpdt)_2]^{2-}$	– [c]	–	– [c]	–	2.8×10^{-6} [g]	–	–
$[Ni^{II}(qdt)_2]^{2-}$	– [c]	2.2×10^{-4} [d]	2.2×10^{-4}	0.99 [f]	2.8×10^{-6} [h]	–	–
$[Fe(CN)_6]^{3-}$	4.1×10^{-4}	–	– [e]	–	7.2×10^{-6} [i]	7.6×10^{-6}	22
Methylene Blue	3.8×10^{-4}	–	3.6×10^{-4}	1.03	6.3×10^{-6} [j]	6.3×10^{-6} [j]	23

[a] Determined in aqueous solutions.

[b] Determined in DMF solutions.

[c] Values not determined directly due to the adsorption of the compound over the electrode surfaces.

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

[e] Values not determined due to the low solubility of the compounds.

[f] Calculated from the reported values.[24]

[g] Suggested to be approximately equal to $[Ni^{II}(qdt)_2]^{2-}$.

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

[i] $D_{calcd}([Fe(CN)_6]^{3-}) = D_{ref}(MB) \times \{x_{obs}(H_2O, [Fe(CN)_6]^{3-})/x_{obs}(H_2O, MB)\}^{3/2}$

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

As summarized in Table S1, the ratio of the kinematic viscosities of H_2O and DMF (i.e., $\left(\nu_{H_2O}/\nu_{DMF}\right)^{-1/6}$ = 0.99)[24] was used to estimate the $x_{calcd}(H_2O)$ value of $[Ni^{II}(qdt)_2]^{2-}$ (see the footnote *d* for Table S1). To the contrary, the $\left(\nu_{H_2O}/\nu_{DMF}\right)^{-1/6}$ value could be experimentally determined as 1.03 using the $x_{obs}(H_2O)$ and $x_{obs}(DMF)$ values observed for Methylene Blue in our experiments, confirming the validity of our approach. All D_{calcd}'s were estimated from the ratio between $\{x_{obs}(H_2O)\}^{3/2}$ using the D_{ref} value reported for Methylene Blue[23] as a benchmark (see also the footnote *j* for Table S1). Furthermore, as summarized in Table S1, the validity of our method

can be further confirmed by the fact that the D_{calcd} value (7.2×10^{-6} cm^2 s^{-1}), estimated for $[Fe^{III}(CN)_6]^{3-}$ using the above method, matches well with its D_{ref} value (7.6×10^{-6} cm^2 s^{-1}).[22] On the basis of these observations, we decided to adopt the $D_{calcd}(H_2O)$ value of $[Ni^{II}(qdt)_2]^{2-}$ (2.8×10^{-6} cm^2 s^{-1}) as an approximated value of D_{calcd} for $[Ni^{II}(dcpdt)_2]^{2-}$ in order to estimate the TOF value for the HER.

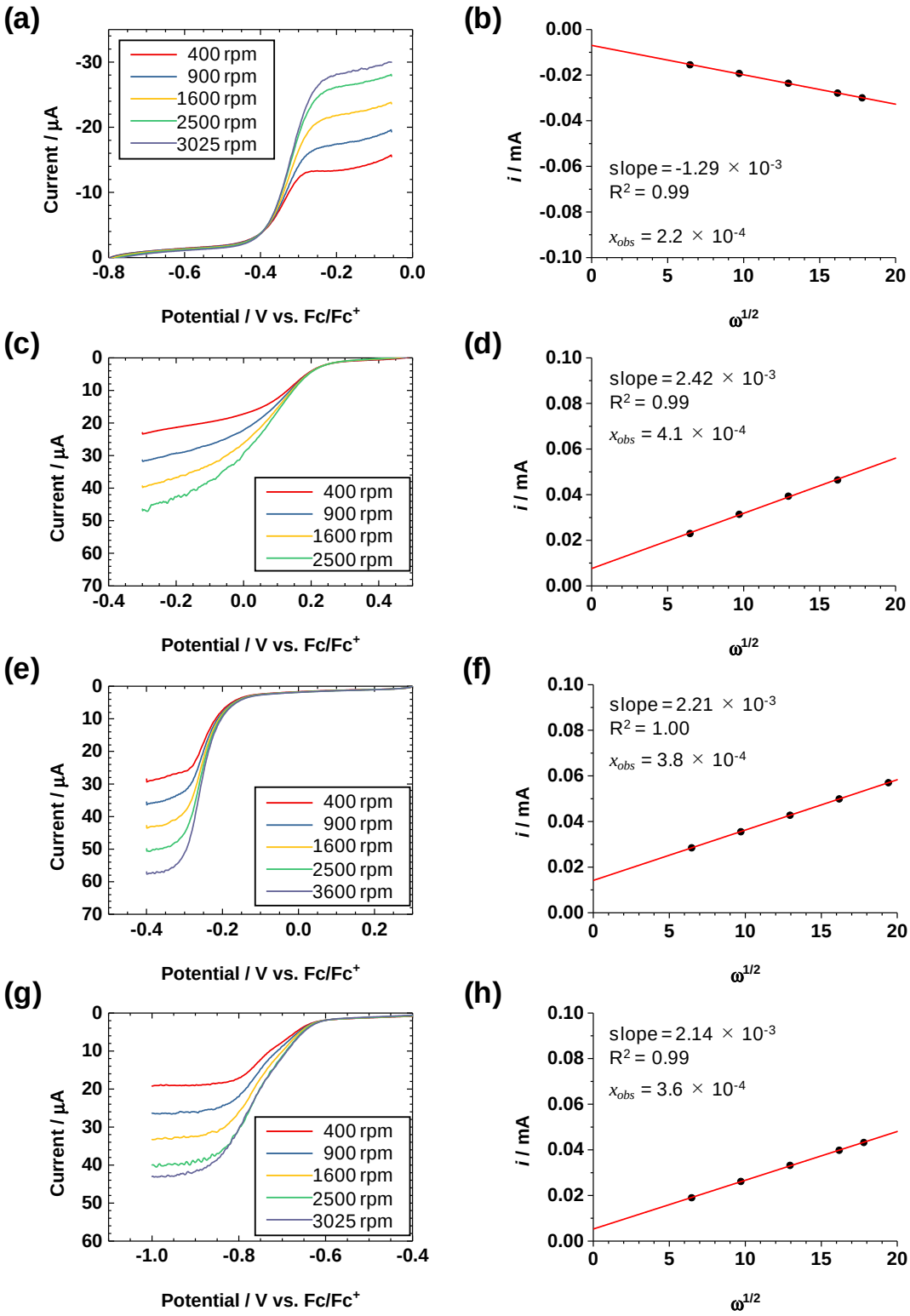


Figure S1. (a,b) LSVs of 0.5 mM $[Ni^{II}(qdt)_2]^{2-}$ in DMF and the plots of the limiting current versus $\omega^{1/2}$. **(c,d)** LSVs of 0.5 mM $[Fe^{III}(CN)_6]^{3-}$ in water and the plots of the limiting current versus $\omega^{1/2}$. **(e,f)** LSVs of 0.5 mM Methylene Blue in water and the plots of the limiting current versus $\omega^{1/2}$. **(g,h)** LSVs of 0.5 mM Methylene Blue in DMF and the plots of the limiting current versus $\omega^{1/2}$.

Determination of the Gibbs free energy of activation ($\Delta G^{\ddagger}_{exp}$)

The Gibbs free energy of activation ($\Delta G^{\ddagger}_{exp}$) of $[Ni^{II}(dcpdt)_2]^{2-}$ was determined by using following eq. 4 (Eyring-Polanyi equation),[25]

$$k = \frac{\kappa k_B T}{h} \exp(-\frac{\Delta G^{\ddagger}}{RT}) \qquad (4)$$

where k is the reaction rate constant (= k_{obs}), κ is the transmission coefficient (≈ 1), k_B is the Boltzmann's constant (= 1.380 × 10^{-23} [J K^{-1}]), T is the absolute temperature (298 [K]), h is the Plank's constant (6.626 × 10^{-34} [J s]) and R is the gas constant (8.314 [J K^{-1} mol^{-1}]).

The $\Delta G^{\ddagger}_{exp}$ can be calculated as 16.0, 16.3 and 17.0 kcal mol^{-1} at pH = 4, 5 and 6, respectively.

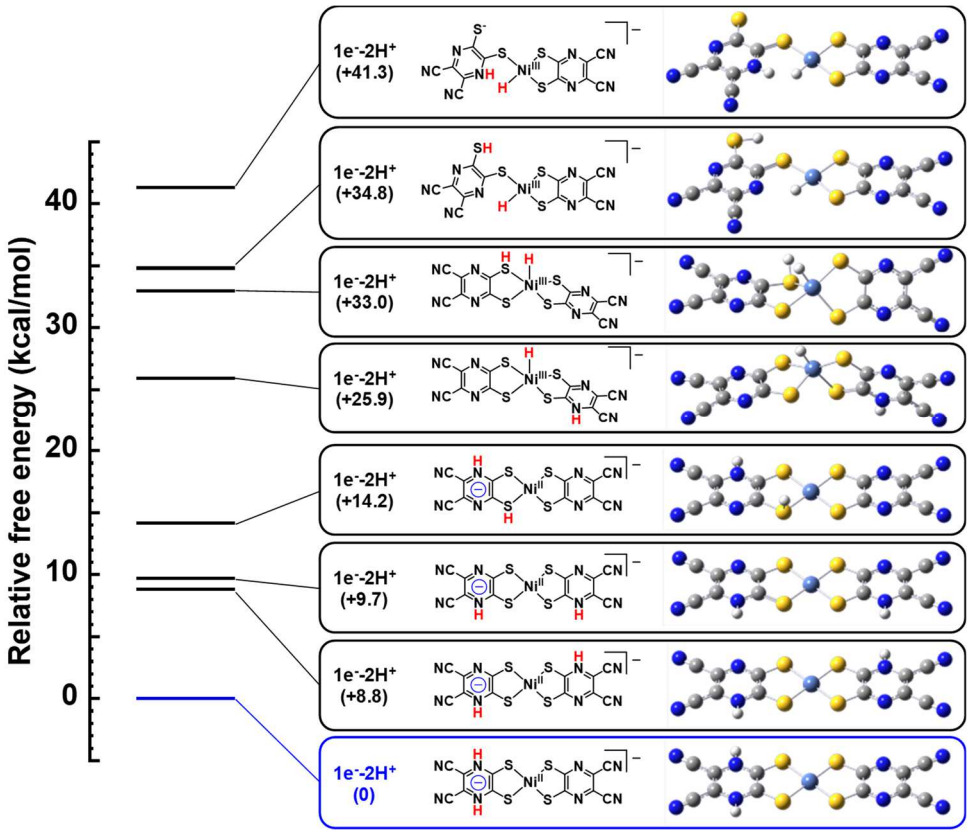


Figure S2. Comparison of free energies for some relevant tautomers computed for the **1e⁻-2H⁺** product.

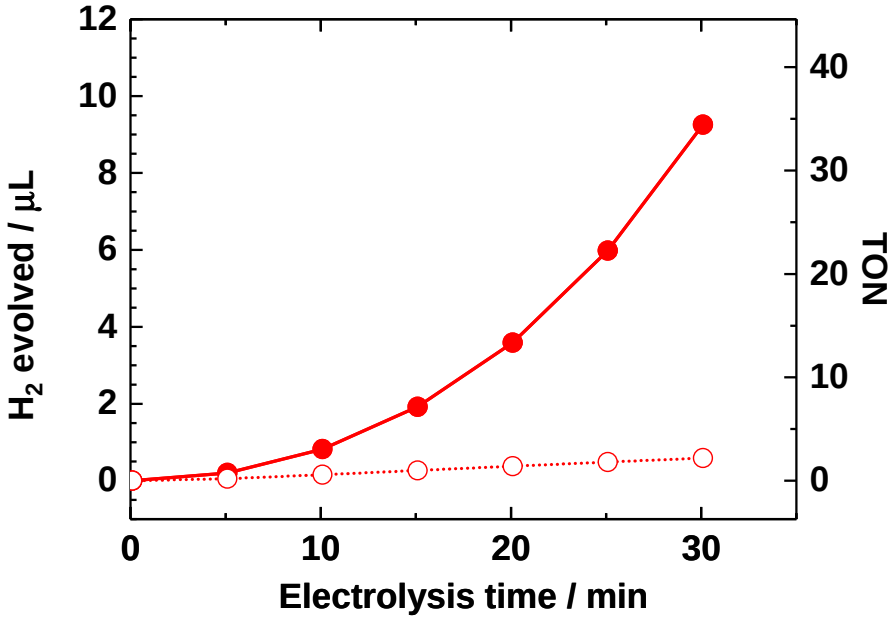


Figure S3. Electrochemical H_2 evolution catalyzed by $Na_2[Ni^{II}(dcpdt)_2]\bullet 4H_2O$ (1 μM) during the controlled potential electrolysis at -1.3 V vs. SCE in an aqueous borate buffer solution (0.1 M; pH 9.0, 12 mL) containing NaCl (0.1 M) under Ar atmosphere. The working, counter, and reference electrodes were a GC rod, a Pt plate, and a SCE, respectively. Applied overpotential = 0.52 V. The results clearly indicate that $[Ni^{II}(dcpdt)_2]^{2-}$ is an active catalyst for HER even at pH =9.0. The gradual raise in the H_2 evolution rate during the electrolysis is attributable to the gradual deposition of the catalyst itself, as previously reported.[17] As discussed in the report,[17] this catalyst tends to be absorbed over the GC surfaces even by simple dipping of the catalyst solution without electrolysis. We also reported that the absorbed species preserve the NiS_4 core based on the energy dispersive X-ray fluorescence spectroscopy (see ref. 17).

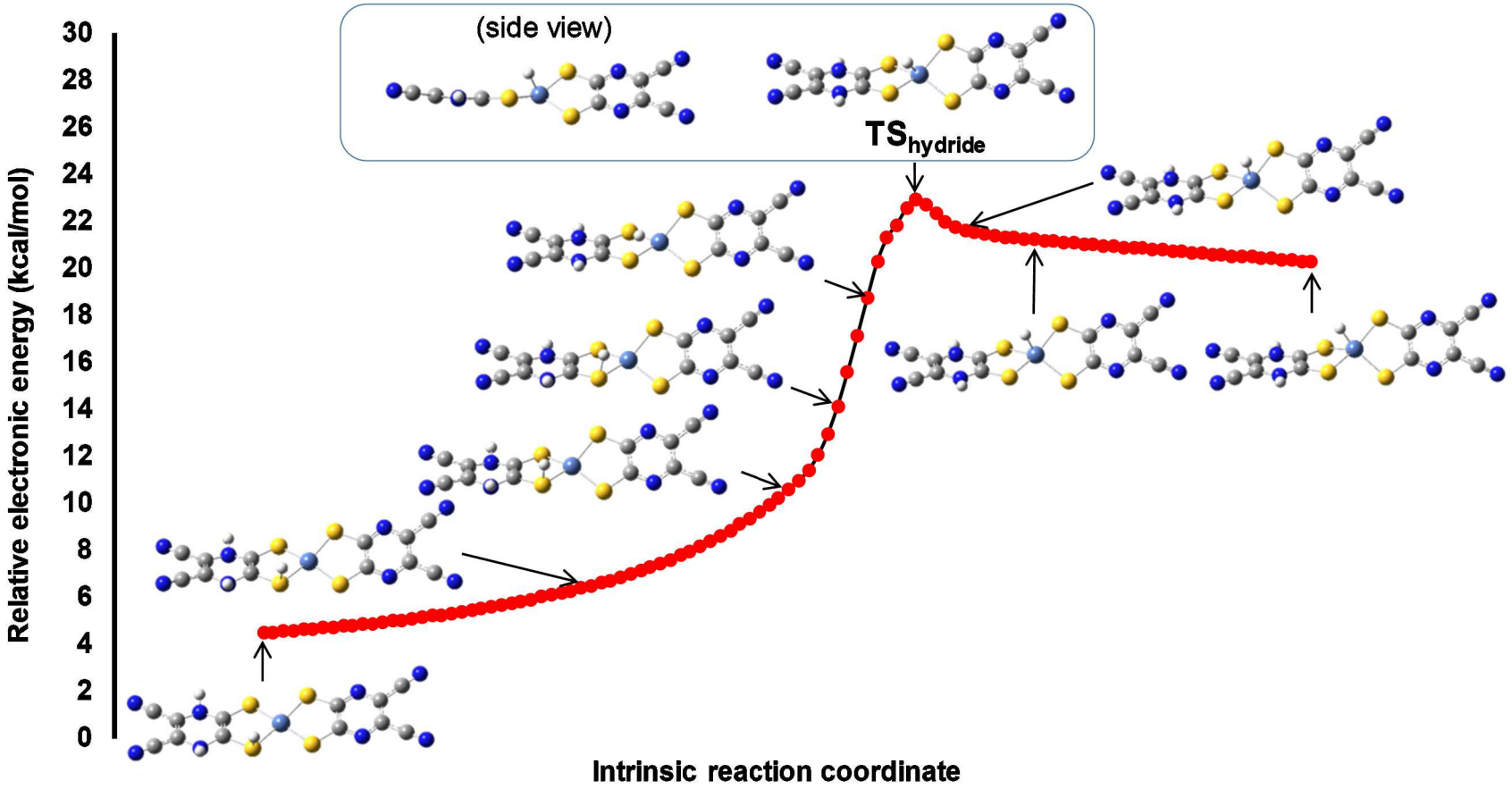


Figure S4. IRC (open-shell singlet) for the transition state of the hydride formation process ($\mathbf{TS_{hydride}}$; $\mathbf{2e^{-}\text{-}3H^{+}}$, +16.6), carried out at UB3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM). In this figure, we adopted relative electronic energy to that of the most stable second PCET product ($\mathbf{2e^{-}\text{-}3H^{+}}$, 0; Figure 3a), rather than its relative Gibbs free energy.

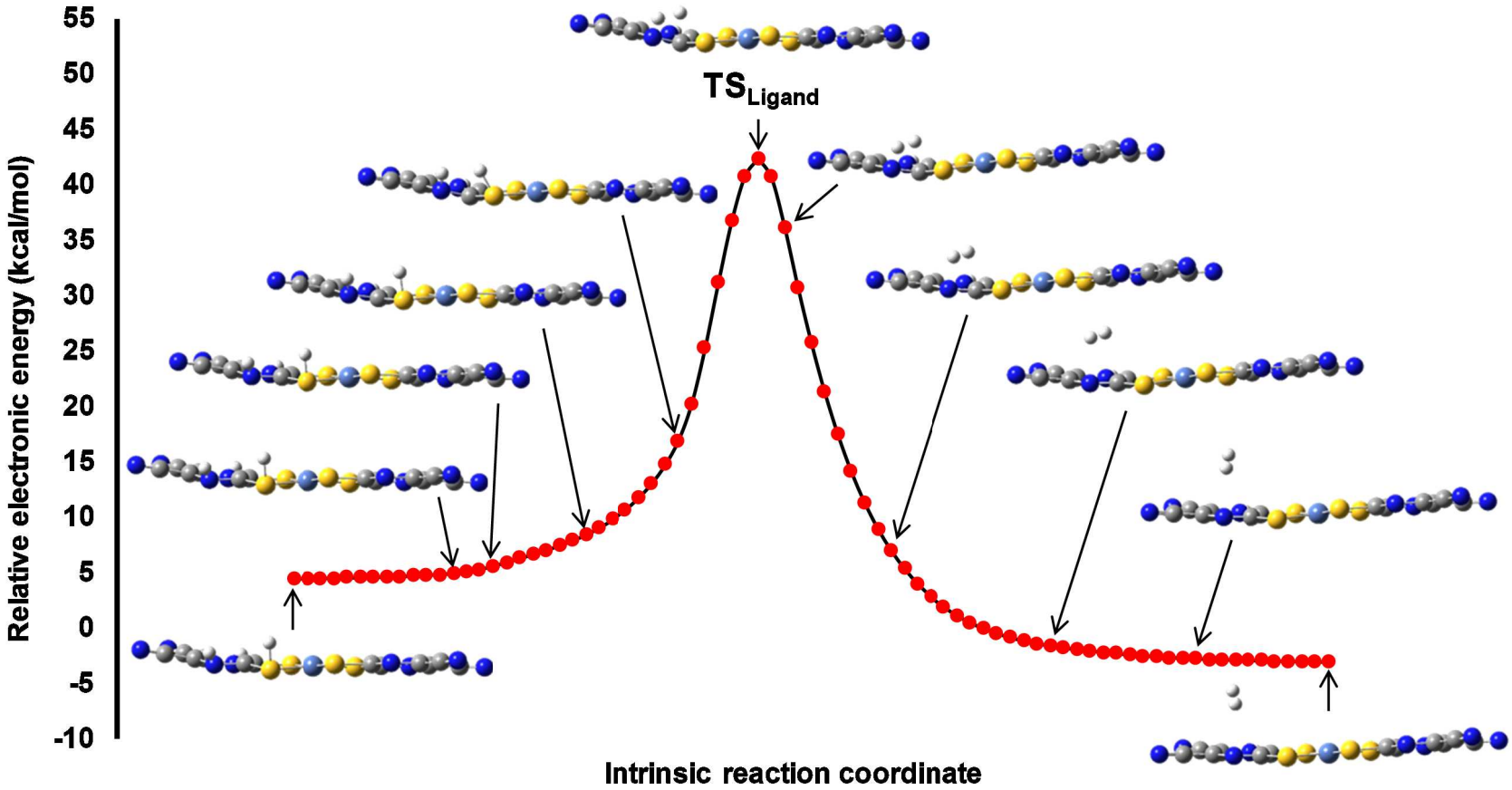
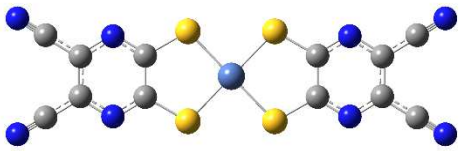


Figure S5. IRC (closed-shell singlet) for the transition state of the ligand-centered H_2 elimination process (**TS$_{ligand}$**; **2e$^-$-3H$^+$**, +36.8), carried out at B3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM). In this figure, we adopted relative electronic energy to that of the most stable second PCET product (**2e$^-$-3H$^+$**, 0; Figure 3a), rather than its relative Gibbs free energy.

Table S2. Geometry optimized for $[Ni^{II}(dcpdt)_2]^{2-}$ (**0e$^-$-0H$^+$**) in its closed-shell singlet state. Optimized at B3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]



Atom	X	Y	Z
N	4.16201839	1.39926537	0.001156
C	3.02635116	0.72055473	0.00053835
C	5.3031352	0.6965148	0.00062786
C	3.0263529	-0.72055663	-0.00054195
C	5.30313662	-0.69651177	-0.00061863
N	4.16202124	-1.39926459	-0.00115349
S	1.52775865	-1.56629845	-0.00108059
S	1.52775633	1.56629378	0.0010678
N	-4.16201932	1.39926525	-0.00115267
C	-3.02635258	0.7205543	-0.00054087
C	-5.3031362	0.69651479	-0.00061942
C	-3.02635366	-0.72055541	0.00053925
C	-5.30313726	-0.69651176	0.00062567
N	-4.16202162	-1.39926436	0.00115501
S	-1.52775918	-1.56629436	0.00107176
S	-1.52775677	1.56629047	-0.00107866
Ni	0.00000248	-0.00000306	-0.00000492
C	-6.52612637	1.43394859	-0.00139535
N	-7.51841039	2.0213934	-0.002024
C	-6.52612891	-1.43394295	0.00140512
N	-7.51841446	-2.02138506	0.00203659
C	6.52612832	-1.43394254	-0.00139506
N	7.51841388	-2.02138461	-0.00202412
C	6.52612515	1.43394896	0.00140926
N	7.51840938	2.02139346	0.00204204

[a]Part of the Gaussian output file

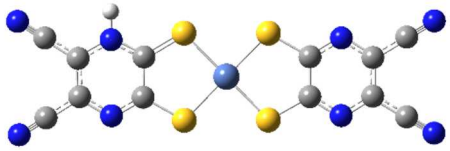
SCF Done: E(UB3P86) = -4001.23783806 A.U. after 1 cycles

	1	2	3
	A	A	A
Frequencies --	12.8334	15.5958	41.2618
Red. masses --	15.0762	17.7348	20.7191

Zero-point correction= 0.110920 (Hartree/Particle)
Thermal correction to Energy= 0.133738
Thermal correction to Enthalpy= 0.134682
Thermal correction to Gibbs Free Energy= 0.054614
Sum of electronic and zero-point Energies= -4001.126918
Sum of electronic and thermal Energies= -4001.104100
Sum of electronic and thermal Enthalpies= -4001.103156
Sum of electronic and thermal Free Energies= -4001.183224

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

Table S3. Geometry optimized for $[Ni^{II}(dcpdt)(dcpdtH)]^{-}$ (**0e^{-}-1H^{+}**) in its closed-shell singlet state. Optimized at B3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]



Atom	X	Y	Z
N	4.17855406	-1.39671462	0.00000228
C	3.04354534	-0.71939347	-0.00001168
C	5.31716019	-0.69248938	0.00002248
C	3.04022244	0.71703228	0.00001589
C	5.31375377	0.70172441	0.00001814
N	4.17163942	1.40014623	0.00002045
S	1.53817292	1.56051074	0.00004472
S	1.5449314	-1.56791373	-0.00006487
N	-4.14452298	-1.33327228	0.00000549
C	-2.95382588	-0.71221702	-0.00003537
C	-5.33473041	-0.65999423	0.00003752
C	-2.98528263	0.73825141	-0.00001549
C	-5.27989919	0.7188747	-0.00000296
N	-4.12726969	1.40514492	-0.00002462
H	-4.15757455	-2.34865519	-0.00000209
S	-1.49977687	1.57092529	0.00002089
S	-1.51103221	-1.56981534	-0.00011231
Ni	0.0254589	-0.00223643	-0.00002798
C	-6.53868427	-1.39754445	0.00012019
N	-7.52664116	-1.99232016	0.00018824
C	-6.49166386	1.47922142	-0.0000309
N	-7.46505196	2.09373452	-0.00005508
C	6.53511148	1.44288871	0.00000982
N	7.52595762	2.03196684	0.00000535
C	6.54220473	-1.42754408	0.00005092
N	7.53598198	-2.01167086	0.00007205

[a]Part of the Gaussian output file

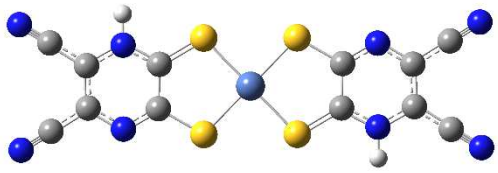
SCF Done: E(RB3P86) = -4001.67221070 A.U. after 13 cycles

	1	2	3
	A	A	A
Frequencies --	14.8280	17.4957	45.4985
Red. masses --	17.0183	13.6229	16.9176

Zero-point correction= 0.124120 (Hartree/Particle)
Thermal correction to Energy= 0.147104
Thermal correction to Enthalpy= 0.148049
Thermal correction to Gibbs Free Energy= 0.068304
Sum of electronic and zero-point Energies= -4001.548099
Sum of electronic and thermal Energies= -4001.525114
Sum of electronic and thermal Enthalpies= -4001.524170
Sum of electronic and thermal Free Energies= -4001.603915

Item	Value	Threshold	Converged?
Maximum Force	0.000069	0.000450	YES
RMS Force	0.000017	0.000300	YES

Table S4. Geometry optimized for [$Ni^{II}(dcpdtH)_2$] (**0e**$^-$-**2H**$^+$) in its closed-shell singlet state. Optimized at B3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]



Atom	X	Y	Z
N	-4.159449	1.334338	-0.000386
C	-2.971839	0.711567	-0.000071
C	-5.349092	0.664743	-0.000336
C	-3.005958	-0.735673	0.000219
C	-5.298425	-0.714984	0.000100
N	-4.145725	-1.400304	0.000356
S	-1.521127	-1.574526	0.000390
S	-1.525538	1.567604	0.000001
N	4.159449	-1.334338	-0.000166
C	2.971839	-0.711567	0.000017
C	5.349092	-0.664743	-0.000221
C	3.005958	0.735673	0.000081
C	5.298425	0.714984	-0.000063
N	4.145725	1.400304	0.000075
H	4.171822	-2.350448	-0.000247
S	1.521127	1.574526	0.000174
S	1.525538	-1.567604	0.000176
Ni	0.000000	0.000000	0.000198
C	6.551687	-1.406380	-0.000439
N	7.538393	-2.002054	-0.000620
C	6.510779	1.474158	-0.000036
N	7.485113	2.086609	-0.000008
C	-6.510779	-1.474158	0.000311
N	-7.485113	-2.086608	0.000489
C	-6.551687	1.406380	-0.000746

N	-7.538393	2.002054	-0.001084
H	-4.171822	2.350448	-0.000638

[a]Part of the Gaussian output file

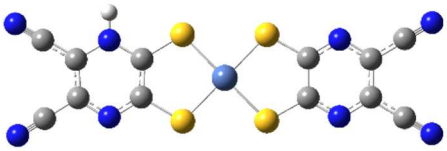
SCF Done: E(RB3P86) = -4002.10088708 A.U. after 2 cycles

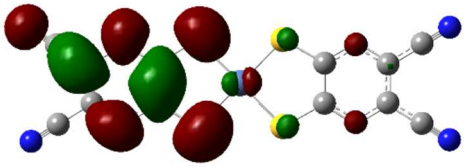
	1	2	3
	A	A	A
Frequencies --	13.0903	16.3776	45.0379
Red. masses --	14.0558	14.9843	16.4957

Zero-point correction= 0.137376 (Hartree/Particle)
Thermal correction to Energy= 0.160572
Thermal correction to Enthalpy= 0.161516
Thermal correction to Gibbs Free Energy= 0.081326
Sum of electronic and zero-point Energies= -4001.963511
Sum of electronic and thermal Energies= -4001.940315
Sum of electronic and thermal Enthalpies= -4001.939371
Sum of electronic and thermal Free Energies= -4002.019561

Item	Value	Threshold	Converged?
Maximum Force	0.000125	0.000450	YES
RMS Force	0.000038	0.000300	YES

Table S5. Geometry optimized for $[Ni^{II}(dcpdt)(dcpdtH)]^{2-}$ (**1e$^-$-1H$^+$**) in its doublet state. Optimized at UB3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]





SOMO

Atom	X	Y	Z	Mulliken spin densities
N	-4.19573626	-1.39761202	0.00668871	0.006878
C	-3.05806655	-0.7215367	0.00275211	-0.000866
C	-5.33525281	-0.69086362	0.00385241	0.000786
C	-3.05427394	0.71995374	-0.00403898	-0.001262
C	-5.33146311	0.7017383	-0.00344648	0.000217
N	-4.18833212	1.40228066	-0.00719819	0.007016
S	-1.5533683	1.56070842	-0.00848883	-0.004731
S	-1.56091631	-1.5683953	0.00604132	-0.003642
N	4.16683002	-1.36836381	-0.00621146	0.25409
C	2.97384243	-0.68565279	-0.00285032	0.164459
C	5.37236968	-0.67038054	-0.00292813	0.238422
C	3.00137961	0.69937854	0.00370376	0.126876
C	5.29202173	0.72145628	0.00377702	-0.095141
N	4.162565	1.41919246	0.00712747	0.16656
H	4.16459278	-2.37707738	-0.00982294	-0.016408
S	1.4955915	1.57210084	0.00833187	0.065739
S	1.50543362	-1.57288568	-0.00720405	0.04809
Ni	-0.02737237	-0.00249689	-0.00029896	-0.00037
C	6.57973917	-1.37398236	-0.00690372	-0.049027
N	7.5777537	-1.96696636	-0.01023704	0.115038
C	6.51120881	1.47681067	0.00756376	0.001744
N	7.48620058	2.09116558	0.01067712	-0.025468
C	-6.55262015	1.44190254	-0.00727704	-0.000192

N	-7.54338522	2.0321086	-0.01032959	0.000622
C	-6.56027571	-1.4244539	0.00870104	-0.000281
N	-7.55413414	-2.00947415	0.01260811	0.00085

[a]Part of the Gaussian output file

SCF Done: E(UB3P86) = -4001.83057302 A.U. after 2 cycles

Annihilation of the first spin contaminant:

S**2 before annihilation 0.7612, after 0.7501

	1	2	3
	A	A	A
Frequencies --	9.2678	17.1438	36.4141
Red. masses --	15.4405	17.5246	19.0598

Zero-point correction= 0.121029 (Hartree/Particle)

Thermal correction to Energy= 0.144769

Thermal correction to Enthalpy= 0.145713

Thermal correction to Gibbs Free Energy= 0.062970

Sum of electronic and zero-point Energies= -4001.709544

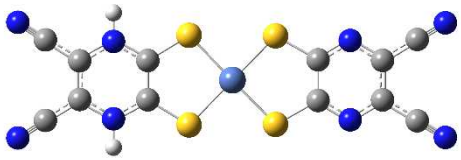
Sum of electronic and thermal Energies= -4001.685804

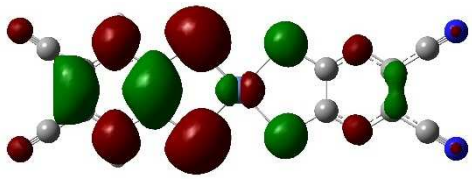
Sum of electronic and thermal Enthalpies= -4001.684860

Sum of electronic and thermal Free Energies= -4001.767603

Item	Value	Threshold	Converged?
Maximum Force	0.000005	0.000450	YES
RMS Force	0.000002	0.000300	YES

Table S6. Geometry optimized for $[Ni^{II}(dcpdt)(dcpdtH_2)]^-$ (**1e$^-$-2H$^+$(0)**) in its doublet state. Optimized at UB3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]





SOMO

Atom	X	Y	Z	Mulliken spin densities
N	4.20711075	1.39906659	-0.0004725	0.008573
C	3.07350127	0.71885697	-0.00024671	-0.002234
C	5.34790084	0.6967829	-0.00022087	0.000674
C	3.07349807	-0.71885283	0.00021919	-0.002234
C	5.34789756	-0.69678926	0.00028204	0.000674
N	4.20710458	-1.39906768	0.00048764	0.008573
S	1.57280539	-1.56263572	0.00043722	-0.00179
S	1.5728113	1.56264577	-0.00052151	-0.00179
N	-4.14176714	1.36388817	-0.00003355	0.1832
C	-2.93272891	0.69305619	-0.00004326	0.202838
C	-5.33483805	0.68206209	0.00001763	0.01158
C	-2.93272574	-0.69305642	0.00000425	0.202838
C	-5.33483514	-0.68207124	0.00005445	0.01158
N	-4.14176144	-1.36389282	0.00004454	0.1832
S	-1.47793919	-1.58047118	0.0000024	0.109972
S	-1.4779459	1.58047956	-0.00008339	0.109972
Ni	0.05226924	0.00000726	-0.00004735	0.004703
C	-6.54183595	1.42006044	0.00002086	-0.007571
N	-7.51525374	2.03779457	0.00002768	0.005157
C	-6.54183097	-1.4200731	0.00008892	-0.007571
N	-7.51524818	-2.03780822	0.00011267	0.005157
C	6.57105045	-1.43450466	0.00060299	-0.000296
N	7.5633042	-2.02152107	0.00085877	0.001041
C	6.57105764	1.43449172	-0.0004926	-0.000296

N	7.56331504	2.02150183	-0.00070836	0.001041
H	-4.14177405	2.37409819	-0.00005003	-0.013495
H	-4.14176494	-2.37410257	0.00008097	-0.013495

[a]Part of the Gaussian output file

SCF Done: E(UB3P86) = -4002.28276955 A.U. after 2 cycles

Annihilation of the first spin contaminant:

S**2 before annihilation 0.7540, after 0.7500

	1	2	3
	A	A	A
Frequencies --	15.2397	16.6528	42.2517
Red. masses --	13.1926	17.5239	15.9978

Zero-point correction= 0.134555 (Hartree/Particle)

Thermal correction to Energy= 0.158494

Thermal correction to Enthalpy= 0.159438

Thermal correction to Gibbs Free Energy= 0.077074

Sum of electronic and zero-point Energies= -4002.148214

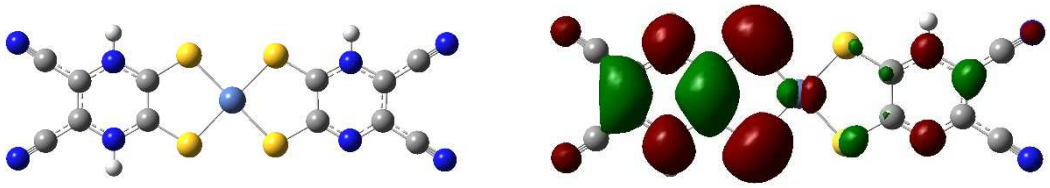
Sum of electronic and thermal Energies= -4002.124276

Sum of electronic and thermal Enthalpies= -4002.123331

Sum of electronic and thermal Free Energies= -4002.205695

Item	Value	Threshold	Converged?
Maximum Force	0.000306	0.000450	YES
RMS Force	0.000036	0.000300	YES

Table S7. Geometry optimized for [Ni^{II}(dcpdtH)($dcpdtH_2$)] (**1e$^-$-3H$^+$**) in its doublet state. Optimized at UB3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]



SOMO

Atom	X	Y	Z	Mulliken spin densities
N	4.19304189	1.33342363	-0.00007844	0.021573
C	3.0025758	0.7130076	0.00002564	0.00647
C	5.38144316	0.65790775	-0.00006294	0.022111
C	3.03216862	-0.73385506	0.00014662	-0.002342
C	5.32473748	-0.72124685	0.00008059	-0.009065
N	4.17047423	-1.40446271	0.00018212	0.031321
S	1.54376163	-1.56518426	0.00023602	-0.017526
S	1.55773483	1.57020944	0.00001297	-0.015791
N	-4.16032909	1.36053551	-0.00017265	0.192379
C	-2.95256846	0.69470651	-0.00005596	0.2004
C	-5.3507802	0.67523172	-0.00019999	0.015281
C	-2.94791835	-0.69114995	0.00001648	0.197253
C	-5.3459849	-0.68895731	-0.00011753	0.016082
N	-4.15064784	-1.36576935	-0.00002154	0.19253
S	-1.48699162	-1.57051554	0.00014099	0.089404
S	-1.49780472	1.58307887	-0.00001083	0.089422
Ni	0.02668774	0.00578471	0.00010644	0.000696
C	-6.56006568	1.41019332	-0.00030947	-0.00857
N	-7.535684	2.02374719	-0.00040091	0.006449
C	-6.54984187	-1.43272412	-0.00011094	-0.008763
N	-7.52086265	-2.0535362	-0.00010344	0.006857
C	6.53493817	-1.48406864	0.00013583	0.000592
N	7.50716765	-2.10014831	0.00018237	-0.00183
C	6.58707314	1.39345507	-0.00018418	-0.004899

N	7.57616908	1.98589013	-0.00028186	0.008575
H	-4.16482696	2.37136157	-0.0002355	-0.013719
H	-4.14818004	-2.3766012	0.00002857	-0.013723
H	4.20858168	2.34909216	-0.00016434	-0.00117

[a]Part of the Gaussian output file

SCF Done: E(UB3P86) = -4002.71358609 A.U. after 2 cycles

Annihilation of the first spin contaminant:

S**2 before annihilation 0.7555, after 0.7500

	1	2	3
	A	A	A
Frequencies --	16.7701	18.5533	44.6575
Red. masses --	16.4867	12.5156	16.1034

Zero-point correction= 0.147944 (Hartree/Particle)

Thermal correction to Energy= 0.171958

Thermal correction to Enthalpy= 0.172902

Thermal correction to Gibbs Free Energy= 0.090891

Sum of electronic and zero-point Energies= -4002.565642

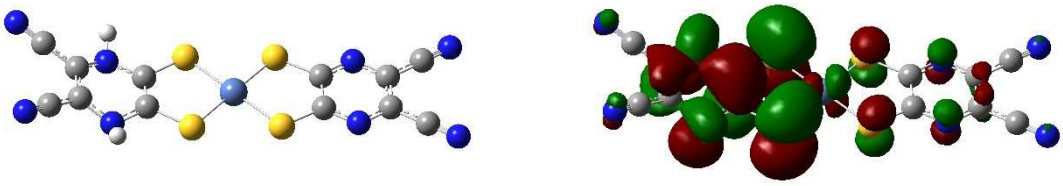
Sum of electronic and thermal Energies= -4002.541628

Sum of electronic and thermal Enthalpies= -4002.540684

Sum of electronic and thermal Free Energies= -4002.622696

Item	Value	Threshold	Converged?
Maximum Force	0.000397	0.000450	YES
RMS Force	0.000045	0.000300	YES

Table S8. Geometry optimized for $[Ni^{II}(dcpdt)(dcpdtH_2)]^{2-}$ (**2e$^-$-2H$^+$**) in its closed-shell singlet state. Optimized at B3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]



HOMO

Atom	X	Y	Z
N	4.22171705	1.3995274	0.05825868
C	3.08517272	0.72083202	0.02917011
C	5.36332043	0.69541547	0.02971879
C	3.08516878	-0.72083339	-0.02914795
C	5.36331657	-0.69542473	-0.02982002
N	4.22170899	-1.39953271	-0.05829669
S	1.58606066	-1.56214823	-0.06324715
S	1.58607004	1.56215211	0.06334488
N	-4.16968301	1.43250714	0.02967998
C	-2.95946443	0.6679606	-0.00315522
C	-5.33959895	0.68032099	-0.02245638
C	-2.9594842	-0.66795759	0.00332482
C	-5.33958016	-0.68032475	0.02236335
N	-4.16965831	-1.4324852	-0.0296165
S	-1.47420545	-1.57879962	0.02087152
S	-1.47419998	1.5788162	-0.02071677
Ni	0.0520283	0.00000577	0.00006876
C	-6.56410044	1.39302491	-0.08091999
N	-7.54336607	2.00169203	-0.13443478
C	-6.56407758	-1.39304943	0.08069393
N	-7.54334067	-2.0017302	0.13410973
C	6.58652131	-1.43079249	-0.06355835
N	7.57892376	-2.01799371	-0.0908794
C	6.58652952	1.43077935	0.06338831

N	7.57893519	2.01797762	0.09065315
H	-4.16267769	2.22642727	-0.60230701
H	-4.16271908	-2.22635832	0.60241476

[a]Part of the Gaussian output file

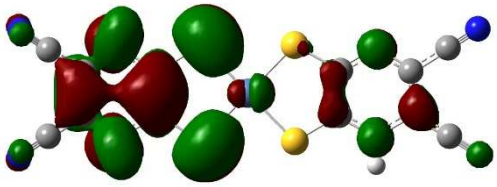
SCF Done: E(RB3P86) = -4002.44296328 A.U. after 2 cycles

	1	2	3
	A	A	A
Frequencies --	9.8623	30.2640	31.7783
Red. masses --	13.0379	10.2934	12.8874

Zero-point correction= 0.134005 (Hartree/Particle)
Thermal correction to Energy= 0.157875
Thermal correction to Enthalpy= 0.158819
Thermal correction to Gibbs Free Energy= 0.077225
Sum of electronic and zero-point Energies= -4002.308958
Sum of electronic and thermal Energies= -4002.285089
Sum of electronic and thermal Enthalpies= -4002.284144
Sum of electronic and thermal Free Energies= -4002.365738

Item	Value	Threshold	Converged?
Maximum Force	0.000017	0.000450	YES
RMS Force	0.000002	0.000300	YES

Table S9. Geometry optimized for $[Ni^{II}(dcpdtH)(dcpdtH_2)]^-$ (**$2e^-$-$3H^+$(0)**) in its closed-shell singlet state. Optimized at B3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]



HOMO

Atom	X	Y	Z
N	-4.1598369	-1.4087196	0.0766087
C	-3.0171245	-0.7341009	0.0150886
C	-5.3080272	-0.7175663	0.1379562
C	-2.9849709	0.7099531	0.0144288
C	-5.3664296	0.6607265	0.1415197
N	-4.1749062	1.3390459	0.0792733
S	-1.5391170	1.5613841	-0.0625450
S	-1.5312359	-1.5626849	-0.0653690
N	4.1971261	-1.3991061	-0.4053765
C	2.9708306	-0.6678970	-0.3041654
C	5.3213072	-0.6839274	0.0096803
C	2.9734766	0.6698684	-0.3026357
C	5.3241984	0.6751942	0.0108637
N	4.2030328	1.3958636	-0.4025049
S	1.4967946	1.5783195	-0.2367352
S	1.4907736	-1.5718910	-0.2410815
Ni	-0.0114096	0.0012923	-0.1466013
C	6.4778681	-1.4116933	0.3778341
N	7.4030288	-2.0356882	0.6732522
C	6.4840752	1.3973141	0.3798371
N	7.4121007	2.0168182	0.6756794
C	-6.5695586	1.3931415	0.2034283
N	-7.5568917	1.9888336	0.2541813
C	-6.5198200	-1.4760207	0.2023602

N	-7.4918026	-2.0910087	0.2543808
H	4.1414832	-2.3354684	-0.0223776
H	4.1514382	2.3319267	-0.0183177
H	-4.1868057	2.3530880	0.0815862

[a]Part of the Gaussian output file

SCF Done: E(RB3P86) = -4002.88204979 A.U. after 1 cycles

	1	2	3
	A	A	A
Frequencies --	16.0838	17.0414	34.5841
Red. masses --	13.5620	14.5331	9.8773

Zero-point correction= 0.146946 (Hartree/Particle)
Thermal correction to Energy= 0.171031
Thermal correction to Enthalpy= 0.171975
Thermal correction to Gibbs Free Energy= 0.089975
Sum of electronic and zero-point Energies= -4002.735104
Sum of electronic and thermal Energies= -4002.711019
Sum of electronic and thermal Enthalpies= -4002.710075
Sum of electronic and thermal Free Energies= -4002.792075

Item	Value	Threshold	Converged?
Maximum Force	0.000012	0.000450	YES
RMS Force	0.000002	0.000300	YES

Table S10. Geometry optimized for **$2e^-$-$3H^+$ (+0.6)** in its closed-shell singlet state. Optimized at B3P86 level of DFT using the 6-311+G(2d, p) basis set with solvation in water taken into consideration (C-PCM).[a]

Atom	X	Y	Z
N	4.2002421	1.4110390	0.0950867
C	3.0787824	0.7176348	0.0138745
C	5.3491734	0.7229592	0.1260432
C	3.0976821	-0.7173936	-0.0397759
C	5.3678445	-0.6693469	0.0722468
N	4.2377513	-1.3841285	-0.0102052
S	1.6092012	-1.5759696	-0.1569951
S	1.5677190	1.5451108	-0.0257174
N	-4.1215039	1.3931432	-0.2422107
C	-2.9318243	0.6437504	-0.1188291
C	-5.3136396	0.7018715	0.0134124
C	-2.9825336	-0.6937461	-0.0423315
C	-5.3487916	-0.6523374	0.0832258
N	-4.2084464	-1.4310534	-0.0887401
S	-1.4903932	-1.5952055	-0.2003604
S	-1.4635803	1.5593308	-0.1794756
Ni	0.0710915	-0.0228070	-0.1330388
C	-6.5004428	1.4644674	0.1223005
N	-7.4482852	2.1152115	0.2235098
C	-6.5769558	-1.3318400	0.2860317
N	-7.5593030	-1.9088929	0.4648070
C	6.5993591	-1.3925164	0.1024561
N	7.5982038	-1.9675178	0.1269442
C	6.5606799	1.4743567	0.2165411
N	7.5436491	2.0720607	0.2900669
H	-4.0700818	2.3263472	0.1483058
H	-4.2100249	-2.2677114	0.4848420
H	-1.3697589	-2.0584941	1.0667299

[a]Part of the Gaussian output file

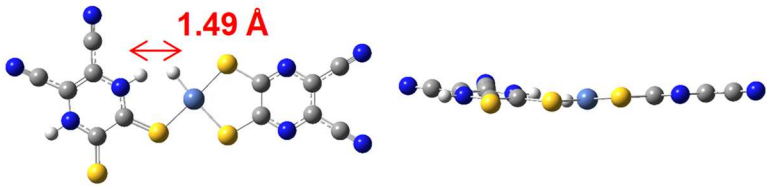
SCF Done: E(RB3P86) = -4002.87531156 A.U. after 2 cycles

	1	2	3
	A	A	A
Frequencies --	1.6216	22.1173	29.7321
Red. masses --	10.3073	11.5796	12.5679

Zero-point correction=	0.143492 (Hartree/Particle)
Thermal correction to Energy=	0.167743
Thermal correction to Enthalpy=	0.168687
Thermal correction to Gibbs Free Energy=	0.084191
Sum of electronic and zero-point Energies=	-4002.731819
Sum of electronic and thermal Energies=	-4002.707569
Sum of electronic and thermal Enthalpies=	-4002.706625
Sum of electronic and thermal Free Energies=	-4002.791121

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

Table S11. Geometry optimized for **2e$^-$-3H$^+$ (+12.3)** in its closed-shell singlet state. Optimized at B3P86 level of DFT using the 6-311+G(2d, p) basis set with solvation in water taken into consideration (C-PCM).[a]



Atom	X	Y	Z
N	4.2973573	-1.2707715	0.1700136
C	3.1550941	-0.6107651	0.0483118
C	5.4309377	-0.5614090	0.1534737
C	3.1485763	0.8248213	-0.0938556
C	5.4234430	0.8262691	0.0145862
N	4.2799763	1.5099068	-0.1076360
S	1.6512600	1.6726663	-0.2501728
S	1.6701010	-1.4790487	0.0608712
N	-3.0862727	0.6453352	0.0088428
C	-2.9206756	-0.6881432	-0.0532583
C	-4.2907894	1.2797255	0.0907729
C	-4.1294680	-1.5298343	-0.0209185
C	-5.4251162	0.5226771	0.1228649
N	-5.3033486	-0.8402760	0.0668269
S	-4.1143609	-3.1726446	-0.0826019
S	-1.3996136	-1.3704857	-0.1618335
Ni	0.1691971	0.1245695	-0.1786960
C	-4.3188182	2.6945101	0.1438416
N	-4.3381727	3.8453070	0.1858129
C	-6.7179136	1.0903581	0.2118623
N	-7.7741714	1.5447178	0.2831372
C	6.6406750	1.5733946	-0.0023291
N	7.6287215	2.1674610	-0.0152845
C	6.6573101	-1.2827172	0.2843808
N	7.6521103	-1.8558297	0.3895484

H	-0.7371807	1.2850701	-0.3605221
H	-6.1450957	-1.4054855	0.0926275
H	-2.1863559	1.1703949	-0.0560521

[a]Part of the Gaussian output file

SCF Done: E(RB3P86) = -4002.85657648 A.U. after 2 cycles

	1	2	3
	A	A	A
Frequencies --	3.8217	23.5212	34.6225
Red. masses --	15.0655	16.3560	15.2965

Zero-point correction= 0.142526 (Hartree/Particle)
Thermal correction to Energy= 0.166445
Thermal correction to Enthalpy= 0.167390
Thermal correction to Gibbs Free Energy= 0.084043
Sum of electronic and zero-point Energies= -4002.714050
Sum of electronic and thermal Energies= -4002.690131
Sum of electronic and thermal Enthalpies= -4002.689187
Sum of electronic and thermal Free Energies= -4002.772533

Item	Value	Threshold	Converged?
Maximum Force	0.000004	0.000450	YES
RMS Force	0.000000	0.000300	YES

Table S12. Geometry optimized for **2e$^-$-3H$^+$ (+14.3)** in its closed-shell singlet state. Optimized at B3P86 level of DFT using the 6-311+G(2d, p) basis set with solvation in water taken into consideration (C-PCM).[a]

Atom	X	Y	Z
N	3.23159779	-0.78273589	-0.0388315
C	3.05092599	0.53060168	0.01817973
C	4.47141584	-1.26716063	-0.08026661
C	4.22162781	1.38412455	0.02920283
C	5.58647283	-0.43573226	-0.06916632
N	5.43821467	0.89473812	-0.01371036
S	4.13738323	3.12799237	0.1001752
S	1.48291683	1.25156765	0.06868907
N	-4.35488064	1.19197382	-0.12509294
C	-3.14805879	0.60521293	-0.04232355
C	-5.53297137	0.50058206	-0.10440782
C	-3.15488322	-0.85106737	0.08032963
C	-5.45372338	-0.87348564	0.00793323
N	-4.29019467	-1.53204087	0.09875744
S	-1.6613756	-1.66837785	0.20046581
S	-1.73669539	1.50804687	-0.08169272
Ni	-0.19420123	-0.1081679	0.11329594
C	-6.748299	1.21226091	-0.19668029
N	-7.74620145	1.78602782	-0.27136358
C	-6.65107506	-1.65559117	0.03133279
N	-7.61304247	-2.28802363	0.05038463
C	6.91380278	-0.95524485	-0.11548452
N	7.98152779	-1.3886688	-0.15317237
C	4.61368143	-2.69135198	-0.13856403
N	4.73989048	-3.83536827	-0.18508294
H	-4.38432224	2.2033834	-0.20744368
H	0.75745319	-1.18737615	0.24794912
H	2.78696226	3.16482376	0.13128137

[a]Part of the Gaussian output file

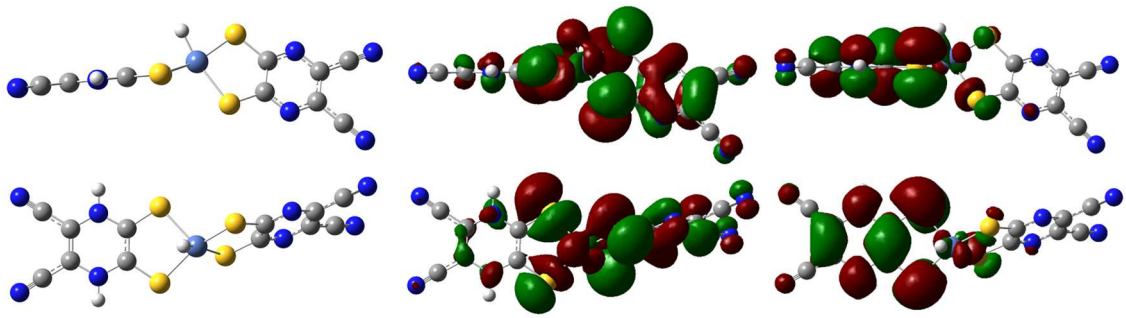
SCF Done: E(RB3P86) = -4002.85014911 A.U. after 2 cycles

	1	2	3
	A	A	A
Frequencies --	11.3242	20.8897	25.6892
Red. masses --	14.1756	17.2555	15.4060

Zero-point correction=	0.139321 (Hartree/Particle)
Thermal correction to Energy=	0.163720
Thermal correction to Enthalpy=	0.164664
Thermal correction to Gibbs Free Energy=	0.080878
Sum of electronic and zero-point Energies=	-4002.710828
Sum of electronic and thermal Energies=	-4002.686429
Sum of electronic and thermal Enthalpies=	-4002.685485
Sum of electronic and thermal Free Energies=	-4002.769271

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

Table S13. Geometry optimized for **2e$^-$-3H$^+$ (+15.5)** in its open-shell singlet state. Optimized at UB3P86 level of DFT using the 6-311+G(2d, p) basis set with solvation in water taken into consideration (C-PCM).[a]



SOMO α SOMO β

Atom	X	Y	Z	Mulliken spin densities
N	-4.2744879	1.0717335	-0.7264723	-0.015752
C	-3.0894296	0.5101563	-0.5642360	0.022118
C	-5.3121045	0.5515187	-0.0610026	-0.000001
C	-2.9237659	-0.6383634	0.2953101	0.005272
C	-5.1544912	-0.5502622	0.7769350	-0.000959
N	-3.9661848	-1.1369721	0.9480768	-0.016144
S	-1.3839193	-1.3816124	0.4798949	-0.012032
S	-1.7496462	1.1923859	-1.4250262	-0.039020
N	3.8928645	1.2347830	0.8073195	0.175495
C	2.7634747	0.5913480	0.3225783	0.161666
C	5.1516607	0.7027165	0.6717205	-0.004994
C	2.9316819	-0.6223469	-0.3449555	0.205449
C	5.3128809	-0.4837557	0.0226884	0.011834
N	4.2132120	-1.1291148	-0.4882397	0.171973
S	1.6416162	-1.5220840	-0.9994261	0.094645
S	1.2482478	1.3174646	0.5699556	-0.033675
Ni	-0.0584911	-0.0497530	-0.7886001	-0.724044
C	6.2525098	1.4083372	1.2114215	-0.002509
N	7.1372531	1.9980796	1.6571940	0.007729
C	6.5879960	-1.0727865	-0.1441810	-0.003438
N	7.6190815	-1.5673810	-0.2910522	0.004050
C	-6.2652927	-1.1010438	1.4887114	0.001125

N	-7.1670612	-1.5380861	2.0582463	-0.002289
C	-6.5870981	1.1687900	-0.2433075	0.000398
N	-7.6207182	1.6596926	-0.3838836	-0.001794
H	3.7709412	2.1046655	1.3053410	-0.014054
H	0.5820363	0.6389691	-1.8783629	0.021129

[a]Part of the Gaussian output file

SCF Done: E(UB3P86) = -4002.85105379 A.U. after 1 cycles

	1	2	3
	A	A	A
Frequencies --	14.1140	19.1870	29.3082
Red. masses --	16.0884	15.9485	12.5471

Zero-point correction= 0.141217 (Hartree/Particle)
Thermal correction to Energy= 0.165806
Thermal correction to Enthalpy= 0.166750
Thermal correction to Gibbs Free Energy= 0.083666
Sum of electronic and zero-point Energies= -4002.709837
Sum of electronic and thermal Energies= -4002.685248
Sum of electronic and thermal Enthalpies= -4002.684303
Sum of electronic and thermal Free Energies= -4002.767388

Item	Value	Threshold	Converged?
Maximum Force	0.000001	0.000450	YES
RMS Force	0.000000	0.000300	YES

Table S14. Geometry optimized for **2e$^-$-3H$^+$ (+20.6)** in its closed-shell singlet state. Optimized at B3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]

Atom	X	Y	Z
N	-3.66861892	1.42139065	-0.73616803
C	-2.79016794	0.46091076	-0.48198365
C	-4.93074543	1.23949859	-0.32680438
C	-3.20012129	-0.74079689	0.21330147
C	-5.32240392	0.08407898	0.34511403
N	-4.4524772	-0.90028005	0.60942823
S	-2.05660239	-1.99633233	0.53080196
S	-1.15771907	0.64698341	-0.98450437
N	4.10145226	-0.23356419	-1.12326436
C	2.89118024	-0.37906746	-0.5098313
C	5.21245277	0.31471262	-0.54199004
C	2.80038953	0.06624568	0.89354867
C	5.13185842	0.74722103	0.7455732
N	3.93871533	0.61283093	1.41067148
S	1.44280768	-0.07678184	1.80601861
S	1.64531901	-1.05800331	-1.3645668
Ni	-0.20524494	-1.24450745	-0.27016601
C	6.4027252	0.40950439	-1.30159253
N	7.3669861	0.48235607	-1.92752589
C	6.23016113	1.32852753	1.42041104
N	7.1175447	1.8046231	1.98044954
C	-6.67041782	-0.09746327	0.77852122
N	-7.76183658	-0.23595932	1.12497759
C	-5.86617709	2.28169652	-0.60746586
N	-6.62808051	3.11834855	-0.83035484
H	4.16970034	-0.55042737	-2.0836838
H	0.28655872	-2.56236937	0.15321369
H	3.88151643	0.92651947	2.37282086

[a]Part of the Gaussian output file

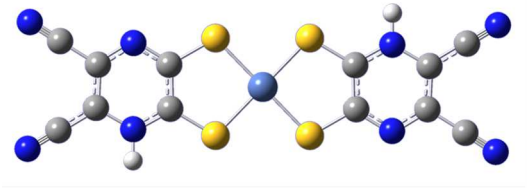
SCF Done: E(RB3P86) = -4002.84371224 A.U. after 1 cycles

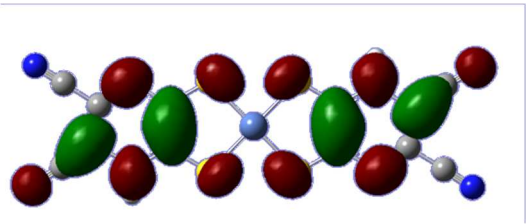
	1	2	3
	A	A	A
Frequencies --	12.4938	16.1062	27.9707
Red. masses --	15.2600	15.7980	12.2439

Zero-point correction=	0.142649 (Hartree/Particle)
Thermal correction to Energy=	0.166894
Thermal correction to Enthalpy=	0.167839
Thermal correction to Gibbs Free Energy=	0.084392
Sum of electronic and zero-point Energies=	-4002.701064
Sum of electronic and thermal Energies=	-4002.676818
Sum of electronic and thermal Enthalpies=	-4002.675874
Sum of electronic and thermal Free Energies=	-4002.759320

Item	Value	Threshold	Converged?
Maximum Force	0.000009	0.000450	YES
RMS Force	0.000002	0.000300	YES

Table S15. Geometry optimized for **1e$^-$-2H$^+$ (+8.8)** in its doublet state. Optimized at UB3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]





SOMO

Atom	X	Y	Z	Mulliken spin densities
N	4.15933572	-1.41008487	-0.00005259	0.145624
C	3.00810316	-0.7140176	-0.00002587	0.049443
C	5.29897856	-0.71430824	-0.00003524	-0.063735
C	2.97563997	0.69911028	0.00001761	0.098574
C	5.36534136	0.66948381	0.00000791	0.147854
N	4.16694682	1.35567702	0.00003214	0.160312
S	1.51543535	1.56239658	0.00005633	-0.015035
S	1.5145774	-1.5635868	-0.00004949	-0.028718
N	-4.16695332	-1.35568944	-0.0000037	0.160442
C	-2.97564309	-0.69910251	0.00000307	0.098668
C	-5.3653521	-0.66948326	0.00000204	0.147972
C	-3.00810268	0.71399972	0.00000595	0.049508
C	-5.29897729	0.71431362	0.00000793	-0.063786
N	-4.15934038	1.41008958	0.00000999	0.145712
H	-4.17219755	-2.36729214	0.00000143	-0.009668
S	-1.51456636	1.56358057	0.00000067	-0.028673
S	-1.51542931	-1.56240136	0.0000109	-0.014998
Ni	0.00000224	-0.00000343	0.00000419	-0.010817
C	-6.57104166	-1.39016817	-0.00000037	-0.032447
N	-7.56375961	-1.98392789	-0.00000171	0.066784
C	-6.5167086	1.46938554	0.00001348	0.003011
N	-7.49167884	2.08216863	0.00001707	-0.016848
C	6.57102806	1.39018349	0.00003187	-0.032424
N	7.56374003	1.98394708	0.00005299	0.066729
C	6.51671077	-1.46937692	-0.00006483	0.003011

N	7.49168244	-2.08215675	-0.00008943	-0.016835
H	4.17219279	2.36728221	0.00005199	-0.009660

[a]Part of the Gaussian output file

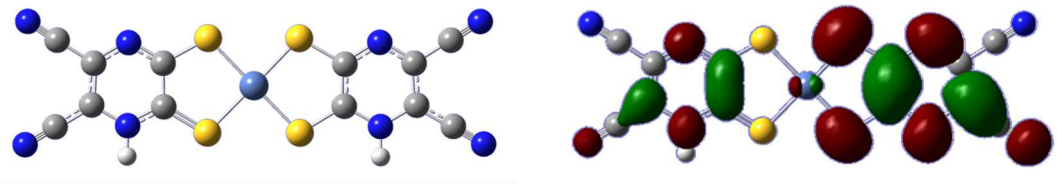
SCF Done: E(UB3P86) = -4002.26693000 A.U. after 1 cycles

	1	2	3
	A	A	A
Frequencies --	-858.7738	16.9947	24.8308
Red. masses --	12.4462	17.6510	12.6587

Zero-point correction=	0.131475 (Hartree/Particle)
Thermal correction to Energy=	0.154976
Thermal correction to Enthalpy=	0.155921
Thermal correction to Gibbs Free Energy=	0.075265
Sum of electronic and zero-point Energies=	-4002.135455
Sum of electronic and thermal Energies=	-4002.111954
Sum of electronic and thermal Enthalpies=	-4002.111009
Sum of electronic and thermal Free Energies=	-4002.191665

Item	Value	Threshold	Converged?
Maximum Force	0.000168	0.000450	YES
RMS Force	0.000052	0.000300	YES

Table S16. Geometry optimized for **1e$^-$-2H$^+$ (+9.7)** in its doublet state. Optimized at UB3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]



SOMO

Atom	X	Y	Z	Mulliken spin densities
N	4.18320864	-1.36239252	-0.00016907	0.238875
C	2.98679878	-0.6923951	-0.00010395	0.158079
C	5.37981822	-0.65793159	-0.00013635	0.217812
C	3.0080145	0.6973423	-0.00001001	0.091731
C	5.29563056	0.73040304	-0.00003995	-0.096438
N	4.1590111	1.42179453	0.00002276	0.194000
S	1.49997456	1.55347195	0.00008324	0.020533
S	1.52219342	-1.576822	-0.00015277	0.021194
N	-4.17713922	-1.33497247	0.00014789	0.057336
C	-2.9822679	-0.7107525	0.00008193	0.029267
C	-5.36618682	-0.65017396	0.00014698	0.054367
C	-3.00612572	0.72978882	0.00001451	0.010719
C	-5.29966586	0.72897043	0.00006538	-0.022413
N	-4.14684131	1.41242522	0.000003	0.061401
H	-4.19404588	-2.3489879	0.00019314	-0.003231
S	-1.51374372	1.55567973	-0.00006433	-0.030624
S	-1.53892653	-1.57417467	0.00008665	-0.021082
Ni	-0.00166563	-0.01329061	-0.00001233	-0.005224
C	-6.57515379	-1.37516067	0.0002341	-0.012365
N	-7.56774156	-1.96435097	0.00030572	0.024043
C	-6.50899923	1.49450421	0.00004321	0.001454
N	-7.47914358	2.11442009	0.00002293	-0.006074
C	6.51054977	1.49238344	-0.00000153	0.002806
N	7.48179545	2.11182977	0.00003137	-0.024187
C	6.5929432	-1.35794899	-0.00021261	-0.046123

N	7.5933748	-1.94326961	-0.00027616	0.099148
H	4.19091525	-2.37191975	-0.00020197	-0.015004

[a]Part of the Gaussian output file

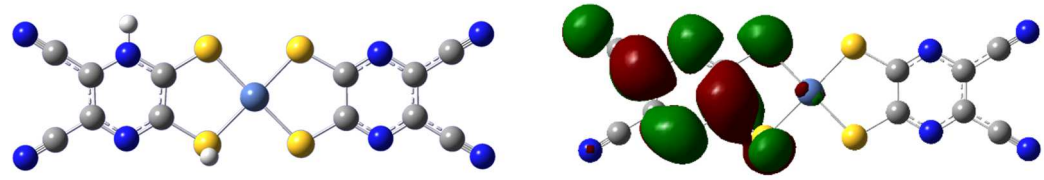
SCF Done: E(UB3P86) = -4002.26737216 A.U. after 1 cycles

	1	2	3
	A	A	A
Frequencies --	17.5820	22.9726	45.2099
Red. masses --	17.5980	12.8338	16.5559

Zero-point correction= 0.133714 (Hartree/Particle)
Thermal correction to Energy= 0.157437
Thermal correction to Enthalpy= 0.158381
Thermal correction to Gibbs Free Energy= 0.077186
Sum of electronic and zero-point Energies= -4002.133658
Sum of electronic and thermal Energies= -4002.109935
Sum of electronic and thermal Enthalpies= -4002.108991
Sum of electronic and thermal Free Energies= -4002.190186

Item	Value	Threshold	Converged?
Maximum Force	0.000065	0.000450	YES
RMS Force	0.000017	0.000300	YES

Table S17. Geometry optimized for **1e$^-$-2H$^+$ (+14.2)** in its doublet state. Optimized at UB3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]



SOMO

Atom	X	Y	Z	Mulliken spin densities
N	4.18352531	1.40646745	0.03149604	0.000430
C	3.05845365	0.71574694	-0.00652011	-0.000167
C	5.33033708	0.71499007	0.04595065	0.000177
C	3.0712883	-0.71888772	-0.03160972	-0.000076
C	5.34296319	-0.67851528	0.01926445	-0.000014
N	4.20877077	-1.3897828	-0.01912221	0.000571
S	1.57700962	-1.57484571	-0.09153361	-0.000298
S	1.54898884	1.54707366	-0.02683654	-0.001407
N	-4.13315597	1.37363108	-0.02321493	0.225595
C	-2.95257878	0.69082095	-0.01973958	0.010976
C	-5.35170737	0.70010606	0.01646493	0.336968
C	-3.03093619	-0.69233862	0.00535578	0.208474
C	-5.30506579	-0.69913503	0.04196823	-0.084937
N	-4.18100461	-1.39928773	0.02891598	0.209371
H	-4.11910731	2.38385695	-0.04205943	-0.013858
S	-1.50952297	-1.59449879	-0.07071807	0.008199
S	-1.48726352	1.56806247	-0.04453922	0.015832
Ni	0.04653089	-0.02172584	-0.05283562	0.001377
C	-6.54159226	1.43431801	0.02470559	-0.078267
N	-7.5268051	2.04529955	0.03055046	0.163605
C	-6.53135189	-1.43720725	0.07985203	0.003598
N	-7.51819787	-2.03047276	0.11013037	-0.028955
C	6.57235434	-1.4061208	0.03083016	0.000083
N	7.56949192	-1.98431793	0.03985874	0.000012
C	6.54633882	1.46361159	0.08947708	-0.000022

N	7.53293805	2.05861921	0.12474448	0.000112
H	-1.45110459	-1.99362565	1.21998657	0.022622

[a]Part of the Gaussian output file

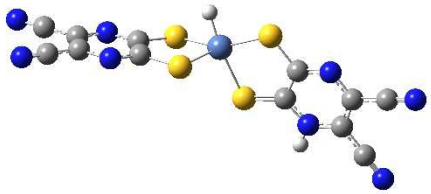
SCF Done: E(UB3P86) = -4002.25721396 A.U. after 37 cycles

	1	2	3
	A	A	A
Frequencies --	16.9424	27.9046	43.9489
Red. masses --	16.7679	13.2500	16.0126

Zero-point correction= 0.130881 (Hartree/Particle)
Thermal correction to Energy= 0.154637
Thermal correction to Enthalpy= 0.155581
Thermal correction to Gibbs Free Energy= 0.074330
Sum of electronic and zero-point Energies= -4002.126577
Sum of electronic and thermal Energies= -4002.102821
Sum of electronic and thermal Enthalpies= -4002.101877
Sum of electronic and thermal Free Energies= -4002.183129

Item	Value	Threshold	Converged?
Maximum Force	0.000123	0.000450	YES
RMS Force	0.000028	0.000300	YES

Table S18. Geometry optimized for **1e$^-$-2H$^+$ (+25.9)** in its doublet state. Optimized at UB3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]



Atom	X	Y	Z	Mulliken spin densities
N1	3.881657	-1.111663	0.892125	0.023799
C2	2.792144	-0.637204	0.258676	0.014469
C3	5.12401	-0.559931	0.781654	0.028908
C4	3.012089	0.544672	-0.571002	-0.015208
C5	5.248942	0.550305	-0.02575	-0.013736
N6	4.21138	1.086431	-0.685142	0.035127
S7	1.704526	1.249991	-1.420001	0.017142
S8	1.303365	-1.383641	0.438646	-0.015194
N9	-3.876864	1.188046	0.953731	0.001263
C10	-2.845827	0.595118	0.366916	-0.020581
C11	-5.094113	0.662415	0.777734	0.007414
C12	-3.054169	-0.584578	-0.446671	-0.037599
C13	-5.291262	-0.472081	-0.002718	-0.006107
N14	-4.267978	-1.083946	-0.611904	-0.001168
S15	-1.736742	-1.408238	-1.19923	0.076682
S16	-1.272621	1.247328	0.614212	0.22677
C17	-6.189613	1.313856	1.424467	-0.000959
N18	-7.079782	1.832486	1.941754	-0.000604
C19	-6.593443	-1.029075	-0.186802	-0.001445
N20	-7.648566	-1.471338	-0.330037	-0.00029
C21	6.523057	1.179832	-0.186245	0.00172
N22	7.547537	1.688292	-0.316612	-0.003123
C23	6.199583	-1.147113	1.485523	-0.007173
N24	7.082888	-1.619611	2.055969	0.012248
H25	3.762986	-1.928622	1.483299	-0.001172
Ni26	-0.033866	-0.005534	-0.854425	0.726982

H27	-0.731483	0.738352	-1.851303	-0.048164

[a]Part of the Gaussian output file

SCF Done: E(UB3P86) = -4002.23816540 A.U. after 2 cycles

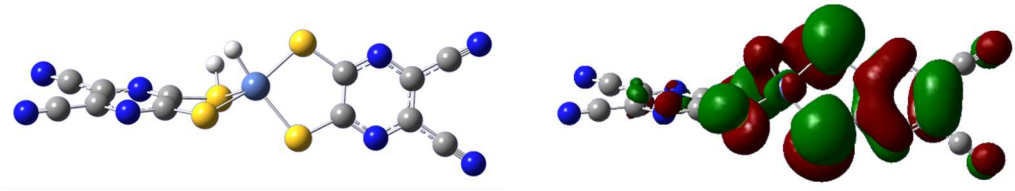
Annihilation of the first spin contaminant:
S**2 before annihilation 0.7705, after 0.7503

	1	2	3
	A	A	A
Frequencies --	15.1933	22.0967	28.8075
Red. masses --	16.2507	16.5028	12.8429

Zero-point correction= 0.130841 (Hartree/Particle)
Thermal correction to Energy= 0.154492
Thermal correction to Enthalpy= 0.155437
Thermal correction to Gibbs Free Energy= 0.073785
Sum of electronic and zero-point Energies= -4002.107324
Sum of electronic and thermal Energies= -4002.083673
Sum of electronic and thermal Enthalpies= -4002.082729
Sum of electronic and thermal Free Energies= -4002.164380

Item	Value	Threshold	Converged?
Maximum Force	0.000003	0.000450	YES
RMS Force	0.000001	0.000300	YES

Table S19. Geometry optimized for **1e$^-$-2H$^+$ (+33.0)** in its doublet state. Optimized at UB3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]



SOMO

Atom	X	Y	Z	Mulliken spin densities
N	4.26713884	-1.18820134	-0.46582177	0.001582
C	3.02774105	-0.75425133	-0.2252453	-0.026177
C	5.28388644	-0.42813251	-0.07750365	0.000863
C	2.86540314	0.46543987	0.50184259	-0.012343
C	5.09909784	0.80190044	0.55772344	-0.004067
N	3.86263284	1.22027187	0.86408888	0.005720
S	1.22061771	0.92495814	1.00477385	0.131979
S	1.69047259	-1.67323503	-0.78499155	0.059046
N	-4.01489286	-1.09446299	0.85930965	0.012292
C	-2.92143996	-0.63566108	0.26485374	0.004437
C	-5.16555392	-0.45348458	0.63855365	0.001354
C	-2.9933556	0.52739135	-0.58308909	-0.007655
C	-5.23257449	0.66419321	-0.19118177	-0.001892
N	-4.14064543	1.14462828	-0.79575774	0.012115
S	-1.58405114	1.16235213	-1.37168198	0.041368
S	-1.42919871	-1.45761226	0.51068602	0.020419
Ni	-0.00388974	-0.17464914	-0.67285161	0.795399
C	-6.3341625	-0.96287112	1.28636866	-0.001746
N	-7.28212512	-1.36551582	1.80333651	0.002302
C	-6.46845896	1.33941467	-0.42992232	-0.000433
N	-7.47103849	1.87654625	-0.61682687	0.001488
C	6.1958144	1.63567922	0.92330896	-0.000542
N	7.0918323	2.3003192	1.21206333	-0.002007
C	6.60473364	-0.92008564	-0.3452876	-0.001688
N	7.66971211	-1.30302133	-0.5541054	0.002446

H	0.74781377	0.5421175	-1.68370227	-0.032799
H	1.35056597	2.23350713	0.71643171	-0.001462

[a]Part of the Gaussian output file

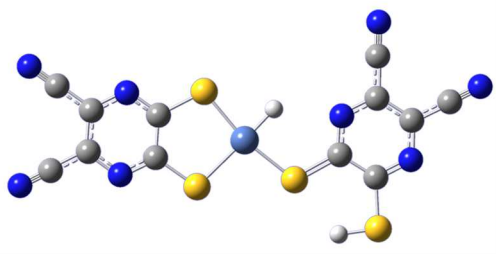
SCF Done: E(UB3P86) = -4002.22339768 A.U. after 29 cycles

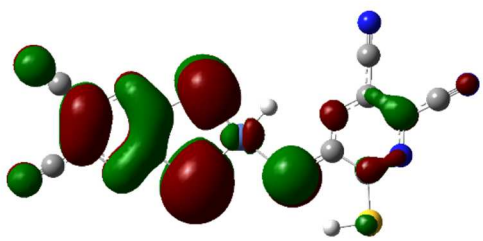
	1	2	3
	A	A	A
Frequencies --	16.2946	21.8416	33.2153
Red. masses --	15.4867	15.7601	13.3276

Zero-point correction= 0.127327 (Hartree/Particle)
Thermal correction to Energy= 0.151032
Thermal correction to Enthalpy= 0.151976
Thermal correction to Gibbs Free Energy= 0.070474
Sum of electronic and zero-point Energies= -4002.096279
Sum of electronic and thermal Energies= -4002.072574
Sum of electronic and thermal Enthalpies= -4002.071629
Sum of electronic and thermal Free Energies= -4002.153132

Item	Value	Threshold	Converged?
Maximum Force	0.000035	0.000450	YES
RMS Force	0.000009	0.000300	YES

Table S20. Geometry optimized for **1e$^-$-2H$^+$ (+34.8)** in its doublet state. Optimized at UB3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]





SOMO

Atom	X	Y	Z	Mulliken spin densities
N	-4.40553624	-1.25212534	0.00467461	0.003716
C	-3.20918083	-0.67226501	0.00574559	0.013662
C	-5.48219904	-0.46710099	-0.00151022	0.020472
C	-3.11073359	0.76383408	0.00036922	-0.020356
C	-5.3799992	0.9241138	-0.00685545	-0.016083
N	-4.18490316	1.52537576	-0.00577882	0.025992
S	-1.56142741	1.56401693	0.00183741	0.091247
S	-1.80472851	-1.66043577	0.01380971	0.013227
N	3.08782633	0.73964926	0.00180516	0.033226
C	3.02134391	-0.57650748	-0.00159937	-0.008520
C	4.27990011	1.33540258	0.00070766	-0.015774
C	4.24308075	-1.33797498	-0.00662558	0.007838
C	5.45585231	0.58954006	-0.00351899	0.027635
N	5.41842964	-0.74270225	-0.00718893	-0.005056
S	4.32247762	-3.08058859	-0.01246486	-0.000493
S	1.49222697	-1.42210928	-0.00030998	0.056861
Ni	-0.1979616	-0.08248607	0.01125898	0.824249
C	4.30315809	2.7656494	0.00405115	0.002366
N	4.33658319	3.9167167	0.00663048	-0.003668
C	6.74060598	1.21678378	-0.00390455	-0.005636
N	7.76830244	1.73646328	-0.00413476	0.011521
C	-6.53923065	1.75737051	-0.01384012	0.002191
N	-7.482131	2.42031084	-0.01948184	-0.002820
C	-6.76057136	-1.11130827	-0.00234229	-0.003641

N	-7.79460572	-1.61900621	-0.00303117	0.008994
H	0.79718401	0.97023227	0.00975595	-0.060302
H	2.98904492	-3.27275427	-0.00948908	-0.000848

[a]Part of the Gaussian output file

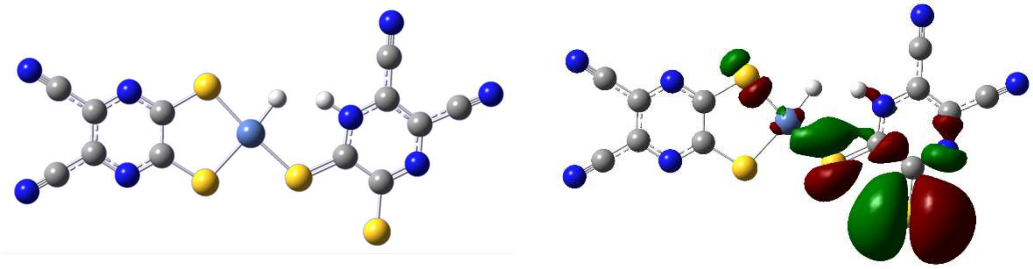
SCF Done: E(UB3P86) = -4002.21959745 A.U. after 3 cycles

	1	2	3
	A	A	A
Frequencies --	-3.3944	18.2489	23.3518
Red. masses --	19.6024	15.2245	15.9052

Zero-point correction= 0.126484 (Hartree/Particle)
Thermal correction to Energy= 0.149820
Thermal correction to Enthalpy= 0.150764
Thermal correction to Gibbs Free Energy= 0.069332
Sum of electronic and zero-point Energies= -4002.093113
Sum of electronic and thermal Energies= -4002.069777
Sum of electronic and thermal Enthalpies= -4002.068833
Sum of electronic and thermal Free Energies= -4002.150265

Item	Value	Threshold	Converged?
Maximum Force	0.000015	0.000450	YES
RMS Force	0.000003	0.000300	YES

Table S21. Geometry optimized for **1e$^-$-2H$^+$ (+41.3)** in its doublet state. Optimized at UB3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]



SOMO

Atom	X	Y	Z	Mulliken spin densities
N	-4.31948233	-1.26930207	0.00024799	0.001948
C	-3.16115886	-0.62002521	0.00012837	0.020376
C	-5.43676817	-0.54416616	0.00011703	0.025723
C	-3.14057122	0.81289161	-0.00007384	-0.023785
C	-5.41072487	0.8522464	-0.00016503	-0.017649
N	-4.25165725	1.51831334	-0.00024093	0.031205
S	-1.63016558	1.68093511	-0.00010405	0.126639
S	-1.69801519	-1.51931581	0.00021986	0.008584
N	3.1720785	0.65833942	0.00006568	0.037629
C	2.99567859	-0.65433466	-0.00004897	-0.001201
C	4.39132586	1.26984421	0.00009049	-0.000257
C	4.19382357	-1.5016967	-0.0001639	0.004509
C	5.49136508	0.42496017	-0.00001733	0.011588
N	5.39967348	-0.89815049	-0.00014281	0.017481
S	4.05497784	-3.17103725	-0.00031355	-0.011767
S	1.43471579	-1.36546131	-0.00005259	0.030808
Ni	-0.17706192	0.11826598	0.00008712	0.764373
C	4.46313538	2.67681125	0.00023661	0.001088
N	4.53667496	3.82862544	0.00036082	0.003026
C	6.81154923	0.98698909	0.00001408	-0.002294
N	7.87088784	1.43641288	0.00004132	0.006779
C	-6.61480637	1.62007799	-0.00038656	0.002294
N	-7.59323335	2.22875869	-0.00056258	-0.002806
C	-6.67841871	-1.2569101	0.00028539	-0.004884

N	-7.68339827	-1.81939764	0.00041981	0.011638
H	2.30903165	1.21857352	0.00014151	-0.003910
H	0.71711421	1.28272287	0.00000158	-0.037133

[a]Part of the Gaussian output file

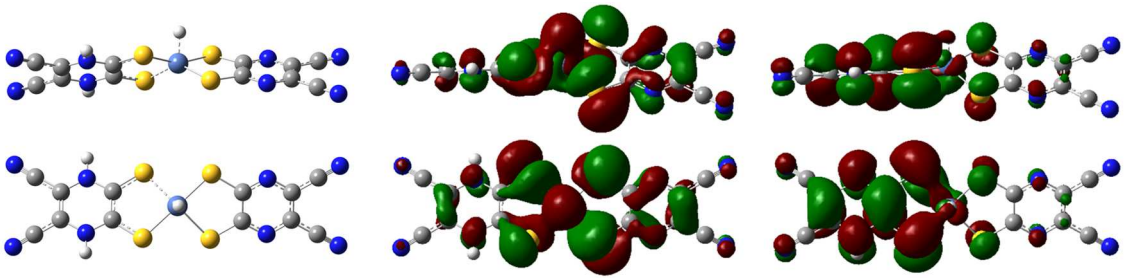
SCF Done: E(UB3P86) = -4002.20450779 A.U. after 37 cycles

	1	2	3
	A	A	A
Frequencies --	13.0296	16.9297	33.5170
Red. masses --	15.4134	17.4772	16.3267

Zero-point correction= 0.130030 (Hartree/Particle)
Thermal correction to Energy= 0.153876
Thermal correction to Enthalpy= 0.154820
Thermal correction to Gibbs Free Energy= 0.071576
Sum of electronic and zero-point Energies= -4002.081371
Sum of electronic and thermal Energies= -4002.057526
Sum of electronic and thermal Enthalpies= -4002.056581
Sum of electronic and thermal Free Energies= -4002.139826

Item	Value	Threshold	Converged?
Maximum Force	0.000003	0.000450	YES
RMS Force	0.000001	0.000300	YES

Table S22. Geometry optimized for the transition state for the H_2 evolution path via the hydride formation process (**$TS_{hydride}$**); **$2e^-$-$3H^+$ (+16.6)** in its open-shell singlet state. Optimized at UB3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]



SOMO α SOMO β

Atom	X	Y	Z	Mulliken spin densities
N	-4.247090	1.255431	-0.513029	0.005835
C	-3.099364	0.634732	-0.294576	-0.029064
C	-5.375715	0.626858	-0.165880	-0.001063
C	-3.069075	-0.699072	0.262088	-0.014837
C	-5.350103	-0.643486	0.404733	0.001380
N	-4.202006	-1.296278	0.611241	0.007709
S	-1.580842	-1.530514	0.483242	0.136475
S	-1.644902	1.484034	-0.675379	0.012464
N	4.141561	1.270654	0.577927	-0.172513
C	2.933622	0.666319	0.265879	-0.171237
C	5.345661	0.641194	0.378592	-0.006290
C	2.958720	-0.632471	-0.243587	-0.176060
C	5.366821	-0.624078	-0.126598	-0.011384
N	4.183116	-1.251580	-0.431612	-0.171798
S	1.549116	-1.487990	-0.662913	-0.085787
S	1.491735	1.528075	0.500981	-0.014427
Ni	-0.062276	0.001747	-0.299435	0.660015
C	6.538283	1.328887	0.705565	0.003293
N	7.498994	1.905082	0.977942	-0.006539
C	6.580805	-1.314922	-0.350094	0.005799
N	7.560068	-1.893064	-0.540072	-0.006760

C	-6.557715	-1.302946	0.791819	0.000218
N	-7.536796	-1.826934	1.101210	-0.000211
C	-6.608166	1.308154	-0.404311	-0.001421
N	-7.608286	1.849728	-0.593295	0.001250
H	4.122079	2.201614	0.968613	0.012831
H	4.202605	-2.164117	-0.863574	0.011171

[a]Part of the Gaussian output file

SCF Done: E(UB3P86) = -4002.84826600 A.U. after 1 cycles

	1	2	3
	A	A	A
Frequencies --	-136.6876	14.9248	26.3141
Red. masses --	1.1676	16.5583	15.5101

Zero-point correction= 0.139326 (Hartree/Particle)
Thermal correction to Energy= 0.163801
Thermal correction to Enthalpy= 0.164746
Thermal correction to Gibbs Free Energy= 0.082601
Sum of electronic and zero-point Energies= -4002.708940
Sum of electronic and thermal Energies= -4002.684465
Sum of electronic and thermal Enthalpies= -4002.683520
Sum of electronic and thermal Free Energies= -4002.765665

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

Table S23. Geometry optimized for the transition state for the H_2 evolution path without hydride formation (**TS_{ligand}**); **$2e^-$-$3H^+$ (+36.8)** in its closed-shell singlet state. Optimized at B3P86 level of DFT using the 6-311+G(2d,p) basis set with solvation in water taken into consideration (C-PCM).[a]

Atom	X	Y	Z
N	-4.166858	1.410677	0.125136
C	-3.046833	0.714848	0.039589
C	-5.317213	0.726541	0.138705
C	-3.070091	-0.718574	-0.031264
C	-5.340105	-0.665769	0.064714
N	-4.212516	-1.382199	-0.019673
S	-1.583171	-1.583566	-0.134824
S	-1.533008	1.536857	0.008143
N	4.046185	1.380210	-0.212902
C	2.936819	0.572335	-0.408409
C	5.224435	0.701004	0.037011
C	2.918608	-0.789258	-0.164824
C	5.274511	-0.663398	0.118346
N	4.125223	-1.403441	0.004597
S	1.466760	-1.671847	-0.043596
S	1.516918	1.488302	-0.384894
N	-0.046736	-0.044967	-0.113251
C	6.408729	1.477227	0.162683
N	7.353789	2.126071	0.281864
C	6.499817	-1.357525	0.289629
N	7.491528	-1.923451	0.442418
C	-6.574499	-1.384991	0.075147
N	-7.575659	-1.956161	0.083456
C	-6.527114	1.480751	0.231270
N	-7.508595	2.080553	0.305628
H	3.583157	2.134517	0.628927
H	4.161303	-2.406638	0.129373

[a]Part of the Gaussian output file

SCF Done: E(RB3P86) = -4002.81458027 A.U. after 1 cycles

	1	2	3
	A	A	A
Frequencies --	-1829.8737	16.1491	31.3311
Red. masses --	1.0768	17.1227	12.1512

Zero-point correction= 0.136425 (Hartree/Particle)
Thermal correction to Energy= 0.159865
Thermal correction to Enthalpy= 0.160810
Thermal correction to Gibbs Free Energy= 0.081070
Sum of electronic and zero-point Energies= -4002.678156
Sum of electronic and thermal Energies= -4002.654715
Sum of electronic and thermal Enthalpies= -4002.653771
Sum of electronic and thermal Free Energies= -4002.733510

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

Table S24. SCF energies given for the model systems optimized at the B3P86/6-311+G(2d,p) level of DFT in either restricted (B3P86) or unrestricted (UB3P86) model under water solvated condition using conductor-like polarizable continuum model (C-PCM) method implemented in the Gaussian 09/16 packages. All the structures given were confirmed as a local minimum structure.

Spin State	Uncorrected SCF Energy (hartree)	Thermal correction to Gibbs Free Energy (hartree)	Sum of electronic and thermal Free Energies (hartree)	Sum of electronic and thermal Free Energies (kcal/mol)	Relative Energy (kcal/mol)	Coordinates
Non-reduced nonprotonated species (**0e$^-$-0H$^+$**)						
closed-shell singlet	-4001.238	0.054614	-4001.183	-2510782.485		Table S2
Non-reduced monoprotonated species (**0e$^-$-1H$^+$**)						
closed-shell singlet	-4001.672	0.068304	-4001.604	-2511046.473		Table S3
Non-reduced diprotonated species (**0e$^-$-2H$^+$**)						
closed-shell singlet	-4002.101	0.081326	-4002.020	-2511307.295		Table S4
One-electron-reduced monoprotonated species (**1e$^-$-1H$^+$**)						
doublet	-4001.831	0.06297	-4001.768	-2511149.189		Table S5
One-electron-reduced diprotonated species (**1e$^-$-2H$^+$**)						
doublet	-4002.283	0.077074	-4002.206	-2511424.096	0.000	Table S6
doublet	-4002.267	0.075265	-4002.192	-2511415.292	8.804	Table S15
doublet	-4002.267	0.077186	-4002.190	-2511414.364	9.732	Table S16
doublet	-4002.257	0.07433	-4002.183	-2511409.935	14.160	Table S17
doublet	-4002.238	0.073785	-4002.164	-2511398.170	25.926	Table S18
doublet	-4002.223	0.070474	-4002.153	-2511391.112	32.984	Table S19
doublet	-4002.220	0.069332	-4002.150	-2511389.313	34.783	Table S20
doublet	-4002.205	0.071576	-4002.140	-2511382.762	41.333	Table S21
One-electron-reduced triprotonated species (**1e$^-$-3H$^+$**)						
doublet	-4002.714	0.090891	-4002.623	-2511685.768		Table S7

Two-electron-reduced diprotonated species (**2e$^-$-2H$^+$**)						
closed-shell singlet	-4002.443	0.077225	-4002.366	-2511524.524		Table S8
Two-electron-reduced triprotonated species (**2e$^-$-3H$^+$**)						
closed-shell singlet	-4002.882	0.089975	-4002.792	-2511792.055	0.000	Table S9
closed-shell singlet	-4002.875	0.084191	-4002.791	-2511791.456	0.599	Table S10
closed-shell singlet	-4002.857	0.084043	-4002.773	-2511779.792	12.263	Table S11
closed-shell singlet	-4002.850	0.080878	-4002.769	-2511777.745	14.310	Table S12
open-shell singlet	-4002.851	0.083666	-4002.767	-2511776.564	15.491	Table S13
closed-shell singlet	-4002.844	0.084392	-4002.759	-2511771.501	20.554	Table S14
open-shell singlet (**TS$_{hydride}$**)	-4002.848	0.082601	-4002.766	-2511775.482	16.573	Table S22
closed-shell singlet (**TS$_{ligand}$**)	-4002.815	0.08107	-4002.734	-2511755.305	36.750	Table S23

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