

Rational Design of Proton-Electron Transfer System Based on Nickel Dithiolene Complexes with Pyrazine Skeletons

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Abstract

To understand the effect of chemical modification on the stability and proton-electron coupling in neutral radical molecules with a proton-electron transfer (PET) state, we investigate a nickel dithiolene complex with cyano-substituted pyrazine skeletons using experimental and theoretical methods. A Pourbaix diagram constructed from absorption spectroscopic and cyclic voltammetric measurements strongly suggests that the PET state of the complex is significantly

more stable compared with that of the non-substituted complex. Theoretical calculations predicted that the introduction of electron-withdrawing groups leads to stabilization of the PET state mainly because of a more delocalized electron distribution in the molecule. Crystallographic studies, with the support of theoretical calculations, revealed that the degree of coupling between protons and electrons varies depending on Hammett's σ value of the substituents; the electronic state of the non-substituted complex appears to be most sensitive to the protonated state mainly owing to the spatially confined π -electron system.

Introduction

A proton-coupled electron transfer (PCET) system has been the subject of intense research in chemistry and biochemistry over the past decades, especially in energy conversion processes.¹⁻³ For instance, a PCET system of hydroquinone/*p*-benzoquinone derivatives is indispensable for electron transportation from photosystems II to I, as well as formation of a proton gradient, which powers ATP production.^{4,5} In solid form, hydroquinone acts as a proton-electron donor (D) while *p*-benzoquinone acts as a proton-electron acceptor (A); these molecules compose a mixed stacked charge-transfer (CT) complex (quinhydrone),⁶ which undergoes a phase transition involving both proton and electron transfers under the application of pressure.⁷⁻¹⁰ The phase transitions on a molecular level are shown in Figure 1. Proton transfer (PT) induces a transformation from a non-transferred (NT) state to a PT state (a), whereas electron transfer (ET) induces a transformation from an NT state to an ET state (c). When the PT and ET occur in a stepwise manner, thus passing through (a)–(b), (c)–(d), or concertedly passing through (e), a transformation from an NT state to a PET state occurs. In this state, D and A molecules

degenerate into identical molecules (semiquinones) and assemble as hydrogen-bonded neutral radicals. From the perspective of physical properties, multi-functionalities including electronic conductivity and magnetism through intra-stack π - π interactions in the ET state and dielectricity through inter-stack hydrogen-bonding interactions in the PT state are expected to be provided in the solid. So far, several degenerate molecular systems have been realized.^{11,12} However, there is no example of π -stacking columns that are connected to each other for constructing an infinite hydrogen-bonding network, which are indispensable for realizing the aforementioned multi-functionalities. A PET-state solid involving such an assembling feature was only realized under high pressure (e.g., 2.5 GPa for quinhydrone), possibly due to the instability of the neutral radical state. To overcome this obstacle, several π -conjugated molecules were synthesized, but none of them shows the PET state under ambient conditions.^{10,13,14} Realization of the PET state under ambient conditions is strongly demanded for a deeper understanding of the physical properties and proton-electron coupled phenomena in the solid.

***** Figure 1 *****

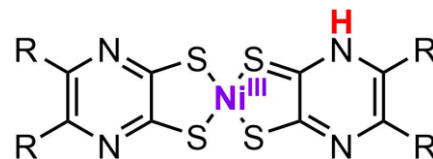
In this study, we focused on nickel dithiolene complexes with pyrazine skeletons.¹⁴⁻¹⁷ They possess multi-redox properties associated with a central nickel atom and protonation/deprotonation properties at nitrogen atoms in the pyrazine skeletons ($pK_b = 13$), as shown in Figure 2. Extension of the π -conjugation throughout the molecule enables the recombination of π -bonds by varying the protonated state, while maintaining the planarity of the molecule.^{14,18-20} When such planar complexes assemble in a π -stacking manner with inter-stack

hydrogen bonds, intermolecular protonation/deprotonation is expected to have a significant effect on the electronic state.

***** Figure 2 *****

As a first step toward establishing a molecular design principal for the stabilized PET state, we performed density functional theory (DFT) calculations²¹ on the PET state of nickel dithiolene complexes with different substituents at the 5,6-positions of

pyrazine moieties, $\text{Ni}^{\text{III}}(\text{HL})(\text{L})$ (L: 5,6-disubstituted-2,3-pyrazinedithiolate). The energy level of singly occupied molecular orbitals (SOMOs) was found to be lowered (stabilized) in the order $\text{R} = -\text{NH}_2, -\text{OH}, -\text{H}, -\text{F}, \text{ and } -\text{CN}$ (Table 1 and Figure S1). A linear relationship between the stability and Hammett substituent constants (Figure 3)^{22,23} clearly indicates that the PET state becomes more stable when the substituents more effectively withdraw electrons, possibly owing to greater delocalization of the electron distribution in the molecule.



***** Table 1 *****

***** Figure 3 *****

Therefore, in this work, we decided to experimentally explore a PET state of the cyano-substituted complex, $\text{Ni}^{\text{III}}(\text{Hdcpdt})(\text{dcpdt})$ ($\text{dcpdt}^{2-} = 5,6\text{-dicyano-2,3-pyrazinedithiolate}$), and assess its electrochemical stability in solution. We also investigated the effect of introducing

cyano-substituents on proton-electron coupling using a newly-synthesized diprotonated complex, $\text{Ni}^{\text{II}}(\text{Hdcpdt})_2$.

Results & Discussion

A non-protonated salt, $(\text{Bu}_4\text{N})_2\text{Ni}^{\text{II}}(\text{dcpdt})_2$ ($(\text{Bu}_4\text{N})_2\cdot\mathbf{1(II)-0H}$; see Figure 2 for the notations), was synthesized according to a literature procedure.²⁴ A diprotonated complex, $\text{Ni}^{\text{II}}(\text{Hdcpdt})_2$ ($\mathbf{1(II)-2H}$), with a composition of $\mathbf{1(II)-2H}\cdot(\text{Et}_2\text{O})_{0.3}(\text{H}_2\text{O})_{0.7}$ determined by elemental analysis and thermogravimetric measurements (Figure S2) was synthesized by the protonation of $\mathbf{1(II)-0H}$ with hydrochloric acid in an acetone solution. Green plate-shaped single crystals of $\mathbf{1(II)-2H}\cdot(\text{Et}_2\text{O})_2$ were grown by vapor diffusion using the crude products (see the Supporting Information for details).

Stability of the PET-state molecule, $\text{Ni}^{\text{III}}(\text{Hdcpdt})(\text{dcpdt})$ ($\mathbf{1(III)-1H}$), in solution. To assess the effect of introducing cyano groups on the stability of the PET-state molecule, we constructed a Pourbaix diagram.²⁵ Although both cyclic voltammetry (CV) and UV-Vis-NIR absorption measurements should generally be performed in an aqueous solution to construct the diagram, we used an acetonitrile solution for the following three reasons: (1) $\text{p}K_{\text{a1}}$ of $\mathbf{1(II)-2H}$ (estimated to be negative) reaches the measurement limit of a commercial pH meter; (2) water has an inadequate electrochemical window for the present CV measurements; (3) $\mathbf{1(II)-2H}$ has low solubility in water. We also chose an anhydrous acid, bis(trifluoromethanesulfonyl)amine (Tf_2NH), because it can work as an acid in organic solvents and the coordination ability of its conjugated base is rather low.

To investigate the protonation equilibrium of $\text{Ni}^{\text{II}}(\text{dcpdt})_2^{2-}$ ($\mathbf{1(II)-0H}$), $\text{Ni}^{\text{II}}(\text{Hdcpdt})(\text{dcpdt})^{1-}$ ($\mathbf{1(II)-1H}$), and $\text{Ni}^{\text{II}}(\text{Hdcpdt})_2$ ($\mathbf{1(II)-2H}$), we performed spectrometric titration of $(\text{Bu}_4\text{N})_2\cdot\mathbf{1(II)-}$

0H in an acetonitrile solution (0.1 mM) containing (Bu₄N)PF₆ (0.1 M) with an addition of Tf₂NH in acetonitrile (0.068 M) (Figure 4). (Bu₄N)PF₆, in which both cation and anion have low coordination abilities, was added in order to perform titration under the same conditions as the CV measurements shown below. During the initial stage, the UV-Vis-NIR spectra show two peaks (418 and 550 nm), which are assigned to transitions from S₀ to S₁₁ and from S₀ to S₆ of **1(II)-0H**, respectively, based on time-dependent DFT calculations (Table S1). Above 1.36 equiv., two additional peaks (612 and 670 nm) appear while the low-wavelength peaks disappear. Because these two peaks were observed for isolated **1(II)-2H** (inset of Figure 4) as S₀ to S₆ and S₀ to S₄ transitions, respectively (Table S2), it is apparent that diprotonated species are generated above 1.36 equiv. There are two noticeable isosbestic points: one at 592 nm between 0 and 1.09 equiv., and the other at 700 nm between 1.22 and 2.86 equiv. The former indicates protonation equilibrium between **1(II)-0H** and **1(II)-1H**, whereas the latter is assigned to that between **1(II)-1H** and **1(II)-2H**. Thus, it is apparent that protonation of **1(II)-0H** occurs consecutively as in the case of non- or ethyl-substituted complexes.^{14,16,17}

***** Figure 4 *****

Next, we performed CV measurements of (Bu₄N)₂·**1(II)-0H** in an acetonitrile solution (0.1 mM) including (Bu₄N)PF₆ (0.1 M) as an electrolyte with an addition of Tf₂NH in acetonitrile (0.068 M). Two events are evident from these measurements (Figure S3). First, there is a reversible redox reaction between Ni(II) and Ni(III) species. Second, an irreversible oxidation from Ni(III) to Ni(IV) species was observed. Consequently, nine kinds of oxidized/protonated states in this complex were electrochemically generated, as shown in Figure 5. Each equilibrium

is distinguished by three types of lines corresponding to three types of equilibria:²⁶ (1) an acid-base equilibrium independent of potential is represented by a vertical red or blue dotted line; (2) a redox equilibrium is represented by a horizontal boundary (filled circle), where only electrons are involved; (3) a redox equilibrium is represented by a slope boundary (open circle), where both protons and electrons are involved.

***** Figure 5 *****

(1-a) **1(II)-0H – 1(II)-1H** and **1(II)-1H – 1(II)-2H**: these equilibria are independent of potential and are represented by red vertical lines at 0.54 and 1.63 equiv., respectively. These lines are determined from the spectrometric titration described above.

(2-a) **1(II)-0H – 1(III)-0H**: this equilibrium only involves electrons and is represented by a horizontal line at $E = \text{ca. } 0.23 \text{ V vs. Ag/Ag}^+$ up to 0.54 equiv.

(3-a) **1(II)-1H – 1(III)-0H**: this equilibrium involves protons and electrons and is represented by a line with slope for 0.54 to 1.22 equiv.

(2-b) **1(II)-1H – 1(III)-1H**: this equilibrium only involves electrons and is represented by a horizontal line at $E = \text{ca. } 0.28 \text{ V vs. Ag/Ag}^+$ for 1.22 to 1.63 equiv.

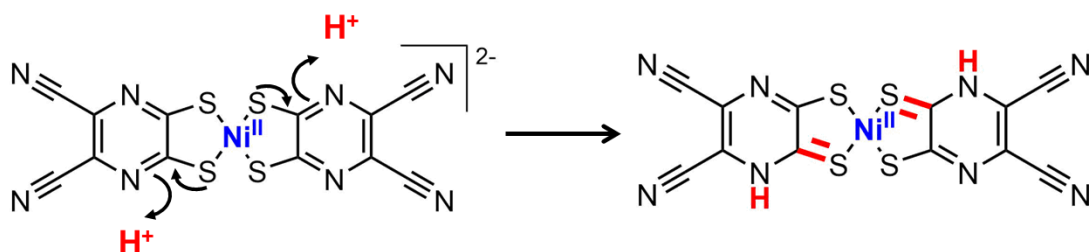
(2-c) **1(II)-2H – 1(III)-2H**: this equilibrium only involves electrons and is represented by a horizontal line at $E = \text{ca. } 0.28 \text{ V vs. Ag/Ag}^+$ above 1.63 equiv.

(2-d) **1(III)-0H – 1(IV)-0H**, **1(III)-1H – 1(IV)-1H**, and **1(III)-2H – 1(IV)-2H**: these equilibria only involve electrons and are represented by a horizontal line at $E = \text{ca. } 0.76 \text{ V vs. Ag/Ag}^+$ for all equiv.

(1-b) **1(IV)-0H – 1(IV)-1H** and **1(IV)-1H – 1(IV)-2H**: these equilibria are independent of the potential and are represented by blue vertical lines at 1.22 and 1.63 equiv., respectively.

The PET-state species, **1(III)-1H**, exists in the orange area in Figure 5. The potential width of this area was estimated to be 0.48 V, which is much larger than the potential width of non- and ethyl-substituted complexes (ca. 0.3 V^{14,27}). These results indicate that introducing cyano groups has a favorable effect on the stability of the PET state, as predicted from theoretical calculations (see Figure 3).

Substituent effect on proton-electron coupling. Complex **1(II)-2H**·(Et₂O)₂ crystallizes in a



monoclinic lattice $P2_1/c$ at 100 K (Table S3).²⁸ Half of a Ni^{II}(Hdcpdt)₂ molecule is crystallographically independent and the central nickel atom is located at an inversion center. Each proton in a Ni^{II}(Hdcpdt)₂ molecule is disordered over two sites with an equivalent occupancy of 0.5. The C-N-C angles and S-C distances in **1(II)-2H**·(Et₂O)₂ are significantly different from those in **1(II)-0H** (Table 2); the C-N-C angles become larger, as expected from valence-shell electron-pair repulsion theory, and the S-C distances become shorter as a result of recombination of π -bonds with protonation. The observation of the N-H bending bands at 1577 and 1626 cm⁻¹ in the infrared spectrum (Figure S4) supports the occurrence of protonation.

***** Table 2 *****

Along the side-by-side direction (a axis), $\text{Ni}^{\text{II}}(\text{Hdcpdt})_2$ molecules are connected to orientationally disordered Et_2O molecules by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds with $\text{N}\cdots\text{O}$ distances of 2.668-2.688 Å (sum of the van der Waals radii: 3.07 Å²⁹) to form the ladder structure (Figure 6a). The complex involves π -stacking columns, in contrast to salts composed of **1(II)-0H**,^{24,30,31} along the b axis (Figure 6b) with an interplanar distance of 3.536 Å in a sliding manner (Figure 6c). Although efforts to chemically isolate the PET-state solid, **1(III)-1H**, have been unsuccessful at present, these crystallographic features suggest that there is some hope of realizing the PET state with π -stacking columns that are connected to each other with hydrogen bonds.

***** Figure 6 *****

To investigate the substituent effect on proton-electron coupling, we compared changes in the bond lengths with protonation between non-substituted and cyano-substituted $\text{Ni}(\text{II})$ complexes (Table 2). Several bonds in the non-substituted complexes are affected greatly by the protonated state; the $\text{Ni}-\text{S}$ and $\text{S}-\text{C}$ bonds shorten by ca. 0.012 and 0.019 Å, respectively, whereas the terminal $\text{C}=\text{C}$ bonds elongate by ca. 0.05 Å. In contrast, most bonds in the cyano-substituted complexes show no significant change with protonation except the $\text{S}-\text{C}$ bonds, which are expected to be greatly affected by the recombination of π -bonds, as mentioned above. Thus, it is apparent that the effect of protonation on the electronic structure is less intense in cyano-substituted complexes than in non-substituted complexes.

We performed DFT calculations for non-substituted and substituted $\text{Ni}(\text{III})$ complexes with different protonated states: $\text{Ni}^{\text{III}}(\text{L})_2^{1-}$, $\text{Ni}^{\text{III}}(\text{HL})(\text{L})$, and $\text{Ni}^{\text{III}}(\text{HL})_2^{1+}$, to investigate the effect of protonation/deprotonation on the electronic structure in the PET-state molecule (Figure S5). As

shown in Figure 7, the difference in the energy level of SOMO by protonation shows a volcano-type dependence on Hammett's σ value of the substituents with an apex at non-substituted complex; namely, the electronic state of the non-substituted complex is most sensitive to the protonated state, which is consistent with crystallographic analyses. It is apparent that the largest decrease in the number of electrons on the π -conjugated plane (excluding proton(s) and substituents) due to protonation (Δ_{π} ; see Table 3), which leads to reduced electronic repulsion, is closely related to the largest proton-electron coupling in the non-substituted complex. However, in the case of cyano-substituted and amino-substituted complexes, the electron deficiency due to protonation occurs at the substituent sites (Δ_R ; see Table 3) in addition to the π -conjugated plane, which suppresses proton-electron coupling. It seems that the smaller variation in the redox potentials with pH in the cyano-substituted complex (Figure 5) compared with that in the non-substituted complex²⁷ is consistent with the theoretical results.

***** Table 3 *****

***** Figure 7 *****

Conclusions

In the present study, the substituent effect on the stability and proton-electron coupling in neutral radical molecules with a PET state were investigated using a nickel dithiolene complex with disubstituted pyrazine skeletons, from experimental and theoretical approaches. Our theoretical calculations revealed that the stability of and proton-electron coupling in the PET state of nickel dithiolene complexes with pyrazine skeletons can be readily controlled by introducing substituents. Indeed, we experimentally succeeded in finding the PET state by introducing cyano

groups, which are expected to yield the most stable PET state owing to the strong electron-withdrawing ability. Whereas the PET state is more stable than that of the reported non-substituted species, proton-electron coupling in the PET state is less effective compared to that of the non-substituted species, possibly due to the extended π -conjugated system. We obtained a new cyano-substituted diprotonated Ni(II) complex involving π -stacking columns, in contrast to the non-protonated complex, which form hydrogen bonds along the side-by-side direction. Therefore, these features strongly suggest that a species formed by protonation and oxidation of the complex (e.g., a neutral radical with the PET state) is a significant target for electronic functional materials. Studies along this line, particularly on the growth of single crystals of the PET-state molecule, are now in progress.

Acknowledgements

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Supporting Information

Experimental details, Kohn-Sham orbitals (Figure S1) and SOMOs (Figure S5) obtained from DFT calculations, thermogravimetric profile (Figure S2), CV spectra (Figure S3), infrared spectra (Figure S4), assignments of low-lying excited states obtained from time-dependent DFT calculations (Tables S1 and S2), bond lengths estimated on the basis of the X-ray diffraction measurement (Table S3).

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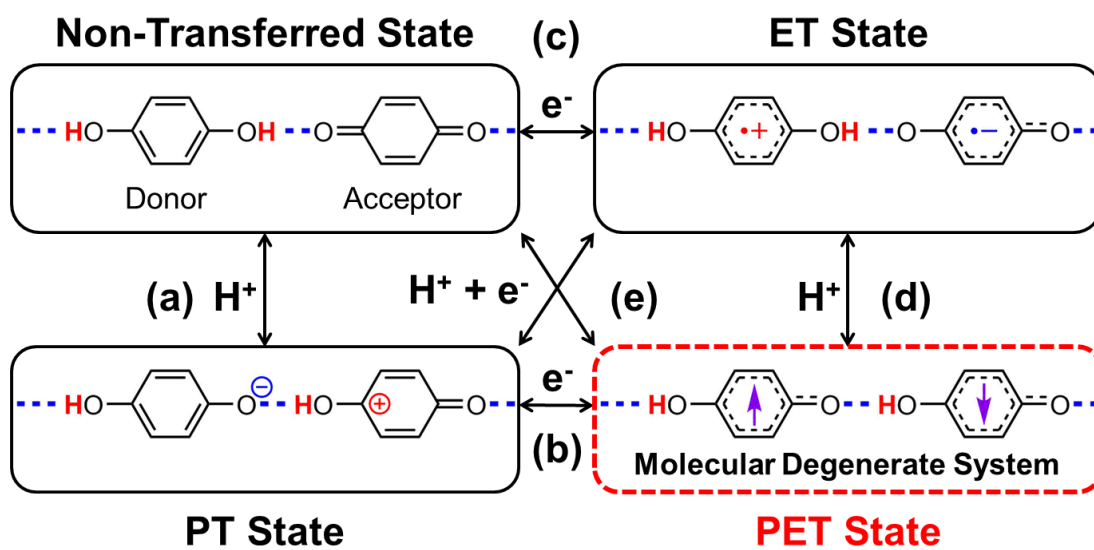


Figure 1. Square diagram for PT, ET, and PET phase transformations of quinhydrone.

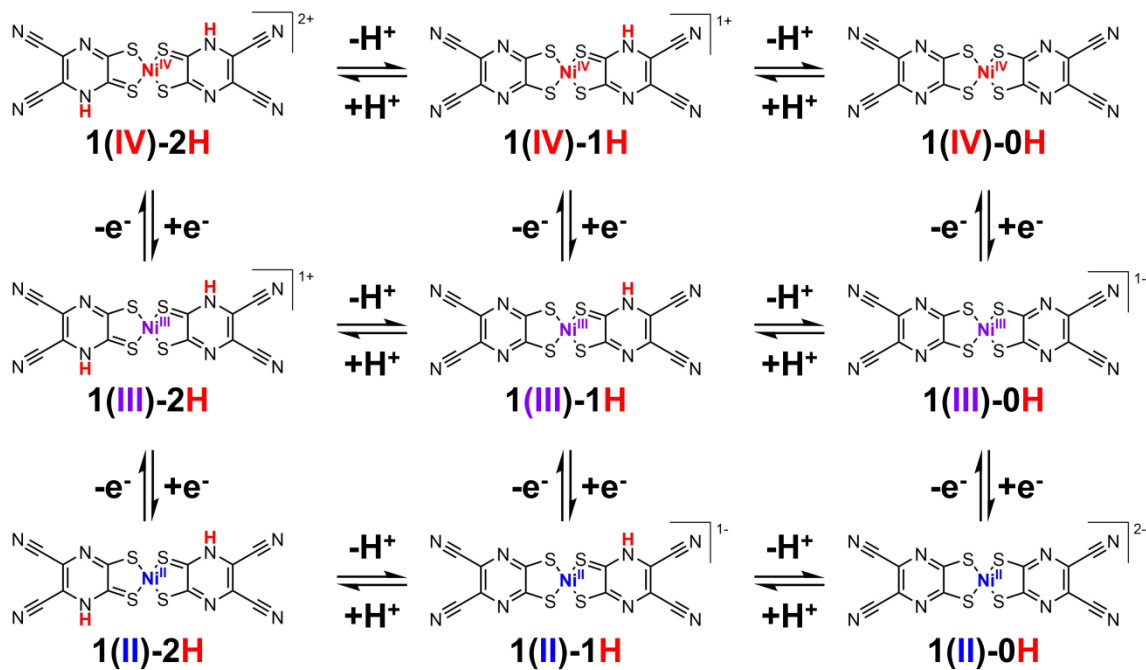


Figure 2. 3×3 (two-proton and two-electron matrix) diagram of a cyano-substituted nickel dithiolene complex system. Each vertical and horizontal arrow corresponds to electron- and proton-transfer, respectively.

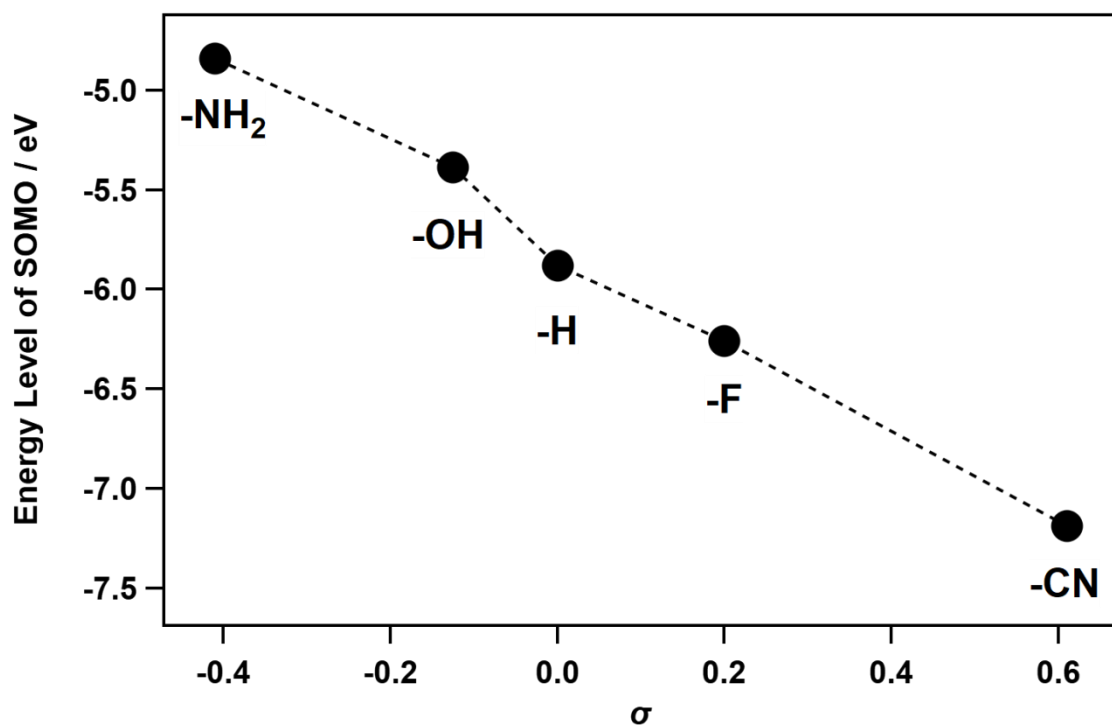


Figure 3. Hammett plot for the energy level of SOMO in $\text{Ni}^{\text{III}}(\text{HL})(\text{L})$ with different substituents, where σ is defined as $(\sigma_{\text{m}} + \sigma_{\text{p}})/2$. A dotted line is shown to guide the eye.

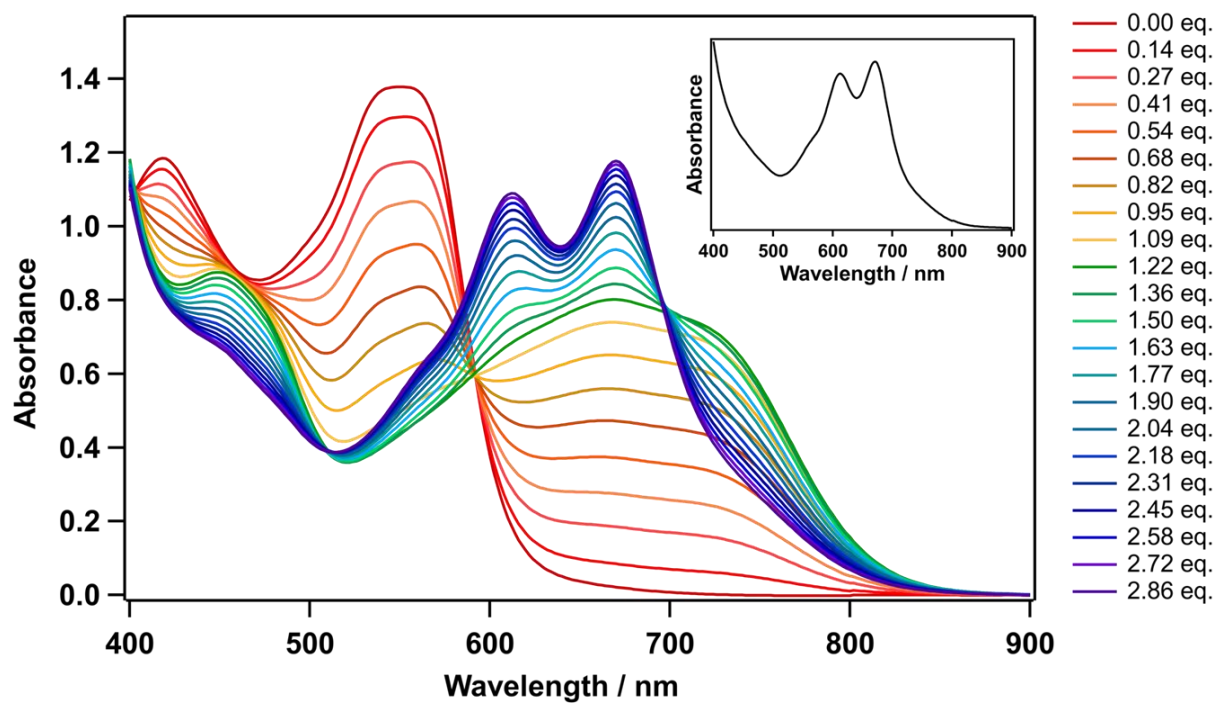


Figure 4. UV-Vis-NIR spectra recorded during the spectrophotometric titration of **1(II)-0H** to **1(II)-2H** via **1(II)-1H** in acetonitrile using Tf_2NH as the titrant. The inset shows the spectrum of isolated **1(II)-2H** in acetonitrile.

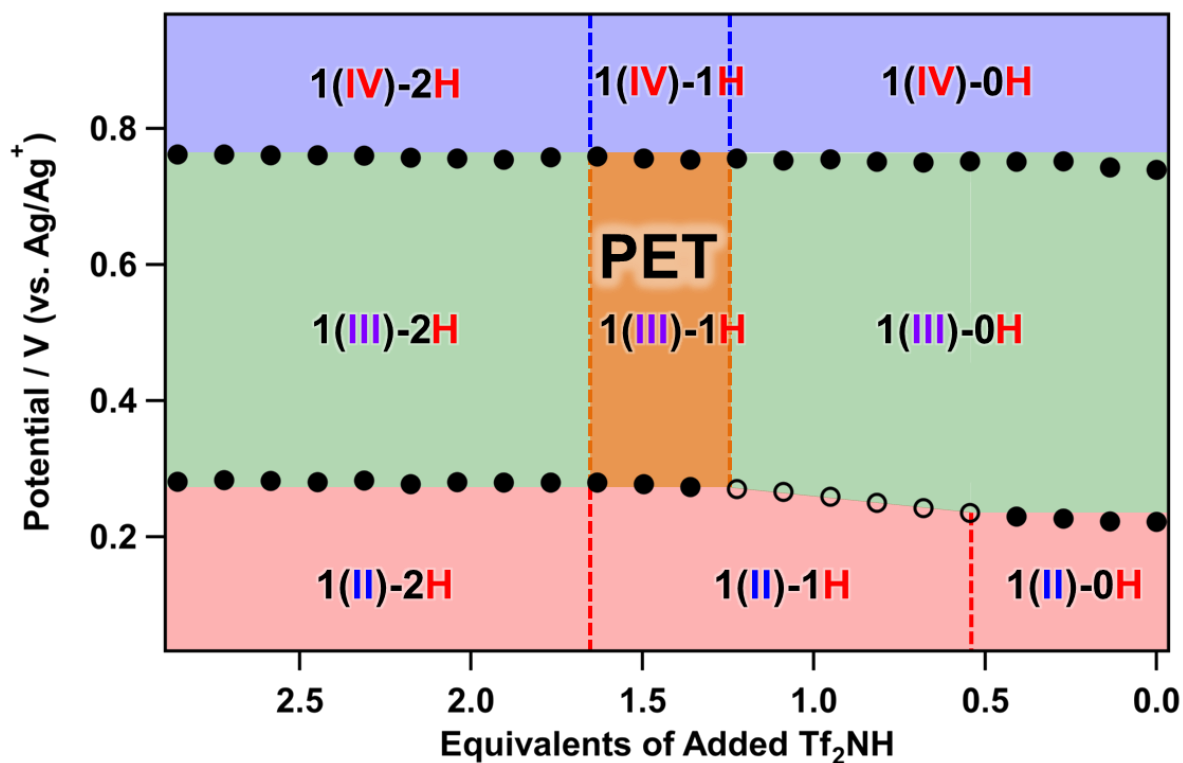


Figure 5. Pourbaix diagram of the cyano-substituted complex. Red and blue dotted lines show the equilibrium (1), whereas filled and open circles represent the equilibria (2) and (3), respectively. Red, green, and blue areas correspond to formal Ni(II), Ni(III), and Ni(IV) oxidation states, respectively. The orange area corresponds to the PET-state molecule, **1(III)-1H**.

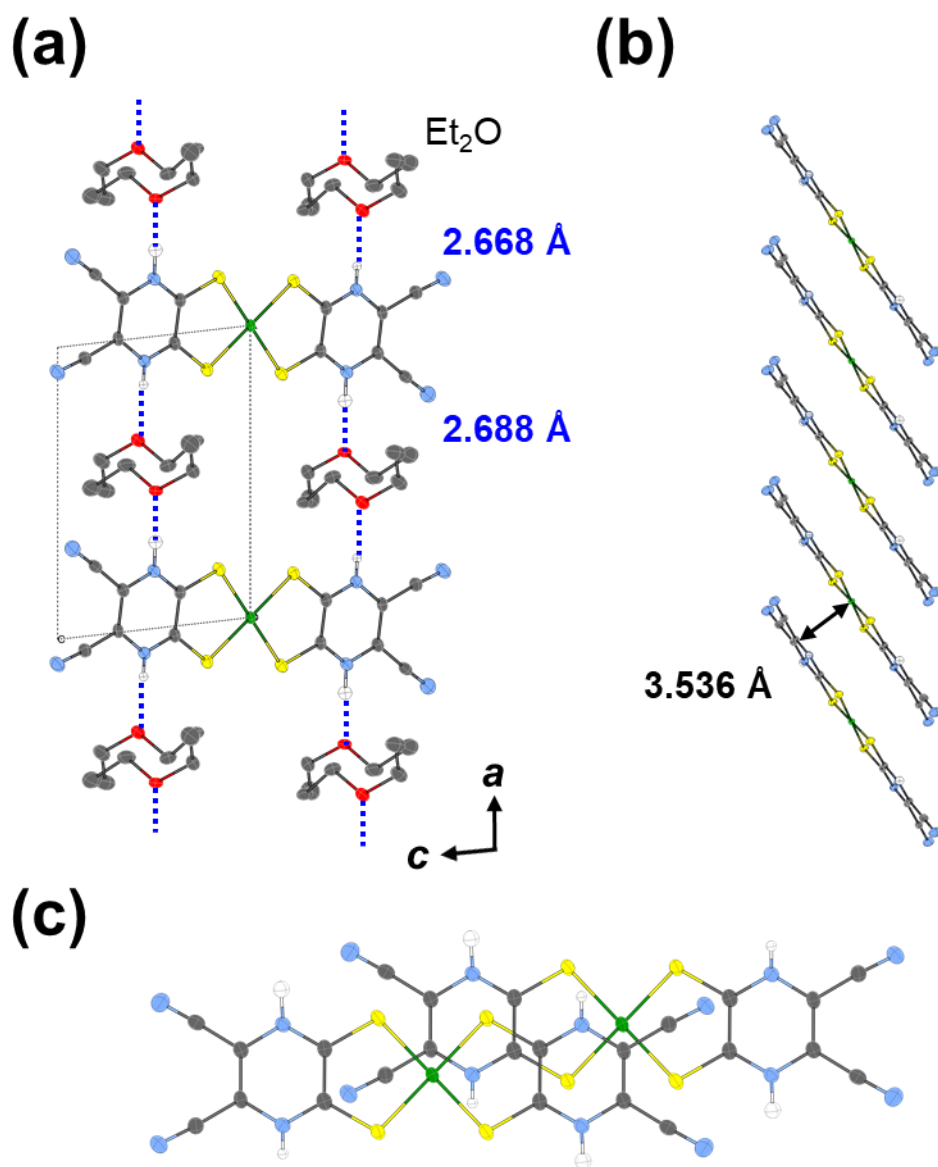


Figure 6. (a) Crystal structure of **1(II)-2H·(Et₂O)₂** (gray: C, white: H, blue: N, green: Ni, red: O, yellow: S) viewed along the *b* axis. Blue dotted lines show N-H···O hydrogen bonds. Hydrogen atoms of Et₂O are omitted for clarity. (b) π -Stacking column of **1(II)-2H** along the *b* axis. (c) Overlap pattern of **1(II)-2H** in the π -stacking column viewed perpendicular to the molecular plane. The 50% probability thermal ellipsoids are shown.

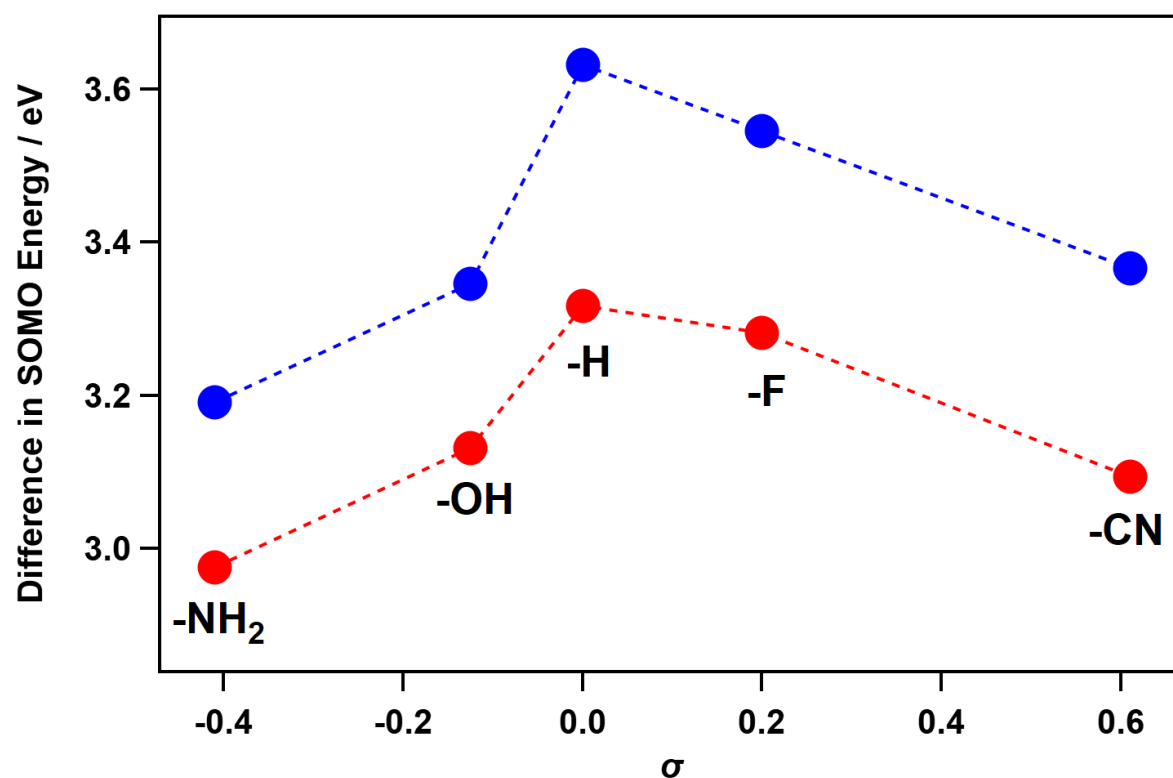


Figure 7. Hammett plots for the difference in the energy level of SOMO of Ni(III) dithiolene complexes with different protonated states. Red and blue circles represent the differences in SOMO energies between mono- and non-protonated states and between di- and mono-protonated states, respectively. The dotted lines are shown to guide the eye.

Table 1. Calculated energy levels of SOMO in Ni^{III}(HL)(L) bearing substituents with different Hammett's σ values

-R	-NH ₂	-OH	-H	-F	-CN
σ^a	-0.41	-0.13	0	0.20	0.61
SOMO / eV	-4.84	-5.39	-5.88	-6.26	-7.19

^a Values are defined as $(\sigma_m + \sigma_p)/2$.

Table 2. Bond lengths of cyano- or non-substituted complexes with different protonated states^a

Average / ° or Å	C-Ni-C	Ni-S	S-C	C=N	N=C	C=C (center)	C=C (terminal)
1(II)-0H @298 K ^b	116.1(1)	2.1722(4)	1.726(1)	1.335(1)	1.352(1)	1.445(2)	1.383(2)
1(II)-2H @298 K	119.2(1)	2.1749(3)	1.706(1)	1.334(2)	1.361(2)	1.454(2)	1.372(2)
Δ	3.2(1)	0.0027(4)	-0.020(1)	-0.001(2)	0.009(2)	0.009(3)	-0.011(3)
Average / ° or Å	C-Ni-C	Ni-S	S-C	C=N	N=C	C=C (center)	C=C (terminal)
Ni ^{II} (pdt) ₂ ²⁻ @298 K ^{b,c}	115.3(2)	2.1755(5)	1.732(2)	1.333(3)	1.349(3)	1.419(4)	1.349(5)
Ni ^{II} (Hpdt) ₂ @296 K ^d	120.7(3)	2.1638(10)	1.713(3)	1.326(4)	1.343(5)	1.425(6)	1.399(8)
Δ	5.4(3)	-0.0118(11)	-0.019(4)	-0.007(5)	-0.007(6)	0.006(7)	0.050(9)

^a Estimated on the basis of the crystallographic data. ^b Data of the Bu₄N salts. ^c Ref. 16. ^d Ref. 27.

Table 3. Differences in the number of electrons on substituted Ni(III) dithiolene complexes with protonation (Δ_{π} : on the π -conjugated plane excluding proton(s) and substituents; Δ_R : on the substituents), calculated based on the natural population analysis

-R	-NH ₂	-OH	-H	-F	-CN
$\Delta_{\pi}(1H-0H)^a$	-0.301	-0.332	-0.391	-0.367	-0.333
$\Delta_{\pi}(2H-1H)^b$	-0.287	-0.313	-0.365	-0.343	-0.307
$\Delta_R(1H-0H)^a$	-0.201	-0.166	-0.109	-0.133	-0.155
$\Delta_R(2H-1H)^b$	-0.198	-0.157	-0.111	-0.128	-0.161

^a Difference between mono- and non-protonated states. ^b Difference between di- and mono-protonated states.

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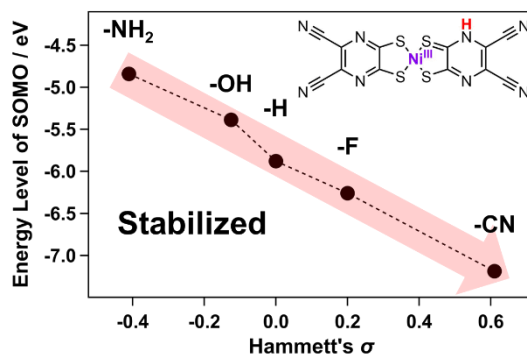


Table of Contents Synopsis

Experimental and theoretical studies revealed that the stability and the proton-electron coupling of a proton-electron transfer (PET) state of nickel dithiolene complexes with pyrazine skeletons can be readily controlled by the introduction of substituents. Cyano-substituted complex is most stable, whereas non-substituted complex is most sensitive to protonated state.