

Isomerization-Controlled Proton–Electron Coupling in a π -Planar Metal Complex

Pingping Huang,[†] Yukihiro Yoshida,^{†} Tokutaro Komatsu,[‡] Yuiga Nakamura,[§] Kunihisa Sugimoto,[§] Hiroshi Kitagawa^{*†}*

[†]Division of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan

[‡]School of Medicine, Nihon University, 30-1 Oyaguchi-Kamicho, Itabashi-ku, Tokyo 173-8610, Japan

[§]Japan Synchrotron Radiation Research Institute (JASRI), SPring-8, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

KEYWORDS

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ABSTRACT

Proton-coupled electron transfer (PCET) is a ubiquitous and fundamental process in biochemistry and electrochemistry performed by transition metal complexes. Most synthetic efforts have been devoted to selecting the components, i.e., metal ions and ligands, to control the proton–electron coupling. Here, we show the first example of controlling the proton–electron coupling using the

cis-trans metal–ligand isomerization in a π -planar platinum complex, Pt(itsq)₂ (itsq¹⁻: *o*-iminothiosemiquinonate). Both the isomers, which were yielded separately, were characterized by single-crystal X-ray diffraction, and the *cis*-to-*trans* isomerization was achieved by immersing in organic solvents. Theoretical calculations predicted that the proton–electron coupling evaluated from the energetic stabilization of the lowest unoccupied molecular orbital by protonation varies greatly depending on the geometrical configuration compared to the metal substitution.

INTRODUCTION

Proton-coupled electron transfer (PCET) process, in which the protonation modulates the electronic (redox) state and vice versa, is critical to energy transformation reactions in natural and artificial systems.^{1–5} In the materials science field, π -electronic molecules that reconstruct the π -conjugation by protonation have been successfully utilized for PCET systems with some unique properties such as ferroelectric behavior associated with quantum proton fluctuations and proton–electron energy-conversion reactions.^{6–15} Metal complexes have attracted significant attention because of their high designability through the diverse combination of plenty of metal ions and ligand molecules. Among them, metal complexes with a π -planar structure are considered a promising source for implementing cooperative coupling between mobile protons and electrons in solids, because the hydrogen-bonding network for proton conduction and the π -stacking column for electronic conduction can be connected through the π -conjugated system.^{16,17} To date, most of the synthetic approaches have focused on the selection of components (I in Figure 1a), i.e., metal ions or ligand molecules, to introduce and control the proton–electron coupling.^{18–30}

Cis/trans isomerization in metal complexes has been a subject of intense research, because of the possible control of electronic state through isomeric transformation.^{31–33} For example, in valence tautomeric (VT) mononuclear cobalt complexes, the *cis* isomer immediately converted to

the *trans* isomer during the course of dissolution in less polar solvents.³⁴ In addition, the *trans* isomer undergoes almost complete VT conversion in the heating process, whereas only about 40% conversion was observed in the *cis* isomer. Another typical system is a luminescence property in two isomers (*syn* and *anti*) of a dinuclear (bipyridine)platinum(II) complex.³⁵ In this system, the *syn* isomer is initially nonemissive but exhibits a red luminescence emission by exposing to acetonitrile or ethanol vapor, whereas the *anti* isomer exhibits very intense orange luminescence. These findings stimulated us to control the proton–electron coupling behavior in metal complexes by the metal–ligand isomerization while keeping the components unchanged (II in Figure 1a).

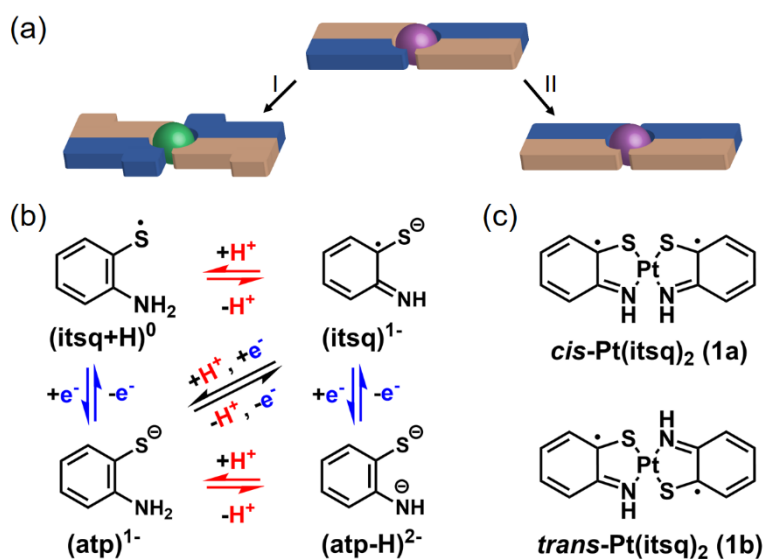


Figure 1. (a) Schematic of the synthetic approaches to control the proton–electron coupling behavior in metal complexes (I: conventional approach which substitutes the metal ion (ball) and/or modifies the ligands (plate); II: our approach which utilizes the metal–ligand isomerization. (b) Proton transfer (red arrows), electron transfer (blue arrows), and proton-coupled electron transfer (black arrows) in a redox-active *o*-aminobenzenethiol ligand. (c) Molecular structures of **1a** (top) and **1b** (bottom).

Very recently, our group found strong proton–electron coupling behavior in a π -planar nickel complex with redox-active N,S-donor ligands, *o*-iminothiosemiquinonate (itsq¹⁻; Figure 1b), in a *trans* geometry.³⁰ In this study, we successfully obtained single crystals of *cis* (**1a**) and *trans* (**1b**) isomers of the platinum complex, Pt(itsq)₂ (Figure 1c), which provided us a promising platform to investigate the effect of the metal–ligand isomerization on the proton–electron coupling. We note that the platinum complexes with redox-active ligands are currently attracting attention as potential catalysts for the hydrogen evolution reaction with a low overpotential.^{23,36,37} Theoretical calculations at the density functional theory (DFT) level revealed that the two isomers have distinctly different proton–electron couplings, which was evidenced by the difference in the energetic stabilization of the lowest unoccupied molecular orbital (LUMO) by protonation. It should be noted that we could experimentally observe the *cis*-to-*trans* isomeric transformation by immersing in organic solvents.

RESULTS AND DISCUSSION

Complex **1a** was obtained as blue thin-plate single crystals by slow evaporation of the acetone solution at room temperature (see the Supporting Information for details). It crystallizes in the monoclinic system with the space group *P*2₁/*c* (Table S1), and one complex molecule is crystallographically independent. As shown in Figures 2a and S1a, the complex molecule has a *cis* configuration with a nearly perfect square planar environment ($\tau_4 = 0.029^{38}$). The C–N bonds ($d_{C1-N1} = 1.330(8)$ Å, $d_{C7-N2} = 1.332(8)$ Å) are shorter than the single bond with imino character, whereas the C–S bond lengths ($d_{C6-S1} = 1.715(7)$ Å, $d_{C12-S2} = 1.720(6)$ Å) fall well within the single bond. Each benzene ring comprises two shorter C–C (1.36(1) – 1.39(1) Å) and four longer C–C (1.41(1) – 1.45(1) Å) bonds so as to form the *o*-semiquinone-type structure. In the crystal, the complex molecules are dimerized in a face-to-face manner with an interplanar separation of 3.49

Å (Figure 2b). The anti-parallel dimer formation on an inversion center results in the cancellation of the dipole moment of each complex molecule (4.009 D based on the calculation at the RB3LYP level of theory). Within the two-dimensional (2D) layer in the *bc* plane, the dimers are arranged in a parallel fashion along the *b* axis with S $\cdots$ S (S1 $\cdots$ S2: 3.66 Å vs van der Waals radii: 3.60 Å³⁹) contacts, whereas C–H $\cdots$ π ⁴⁰ (H2 $\cdots$ π : 2.68 Å; H8 $\cdots$ π : 2.68 Å) interactions connect the dimers with a dihedral angle of 65.2 ° along the *c* axis (Figure S1b).

Complex **1b** was synthesized according to the literature (see the Supporting Information for details).⁴¹ It also belongs to the monoclinic system with the space group *P*2₁/*c* (Table S1) and is isostructural with the nickel-substituent, *trans*-Ni(itsq)₂.⁴² The ligands apparently have the *o*-semiquinone-type structure based on the bond lengths, which are connected by the Pt atom in a perfectly planar manner ($\tau_4 = 0$;³⁸ Figures 2c and S1c). The bonding characters were further verified by IR spectroscopy (Figure S2). The stretching mode of imino N–H bonds was identified

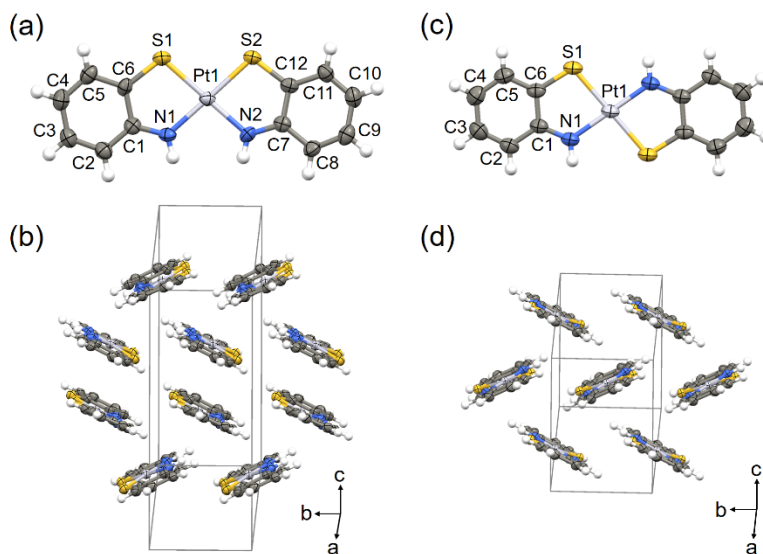


Figure 2. Molecular structures of (a) **1a** and (c) **1b** determined by single-crystal X-ray diffraction analyses. Molecular packing motifs of (b) **1a** and (d) **1b** within the two-dimensional layer (gray, C; white, H; blue, N; yellow, S; silver, Pt).

with the band at 3275 cm^{-1} ,⁴³ whereas the band at 692 cm^{-1} is characteristic of the C–S stretching mode.⁴³ In contrast to **1a**, the complex molecules form a herringbone-like structure in the 2D layer (Figure 2d). The complex molecule interacts with neighboring molecules through N–H $\cdots$ S hydrogen bonds with an H $\cdots$ S distance of $2.97\text{ \AA}$ (sum of van der Waals radii: $3.00\text{ \AA}$ ³⁹) along the *b* axis. Along the oblique direction, on the other hand, C–H $\cdots$ S hydrogen bonding (H2 $\cdots$ S1: $2.94\text{ \AA}$) and S $\cdots\pi$ ⁴⁴ (S1 $\cdots\pi$: $3.41\text{ \AA}$) interactions seem to be a dominant factor in the intermolecular interactions (Figure S1d). Accordingly, the electronic band structures, which were calculated using the Perdew-Burke-Ernzerhof (PBE) functional and projector-augmented-wave pseudopotential on the crystallographic data obtained at 100 K, indicate that energy dispersions in the 2D layer (*// bc* plane) are greater than that along the interlayer direction (*// a* axis) in both **1a** and **1b** (Figure S4).

The cyclic voltammogram (CV) was measured in an acetonitrile solution of **1b** (0.1 mM) containing 0.10 M (Bu₄N)PF₆ as a supporting electrolyte. The measurement for **1a** could not be carried out due to the difficulty in yielding the pure phase and the gradual isomerization to **1b** in organic solvents (see below). Complex **1b** shows two reversible redox couples at $E^1_{1/2} = -0.70\text{ V}$ and $E^2_{1/2} = -1.49\text{ V}$ vs. Fc/Fc⁺, which can be readily assigned to the first reduction from Pt(itsq)₂ to [Pt(itsq)(atp–H)]^{1–} and the second reduction from [Pt(itsq)(atp–H)]^{1–} to [Pt(atp–H)₂]^{2–}, respectively (Figure S5).⁴¹ The square root dependence of the peak current (*i_p*) on the scan rate is firm evidence of the reversible behavior according to the Randles-Sevcik equation (Figures S6 and S7).⁴⁵ Thus, complex **1b** can be regarded as an electron acceptor, in which the ligands are the primary redox center as in Ni(itsq)₂ (Figure 1b).^{30,46,47}

As described above, the different geometrical configurations between **1a** and **1b** are expected to afford not only different proton and/or electronic properties but also different proton–electron coupling properties. To investigate the proton–electron coupling, theoretical calculations of the *cis*

and *trans* isomers with different protonated states were performed at the RB3LYP level of theory. Figure 3 shows the energetic stabilizations of LUMO of **1a** and **1b**, together with *trans*-Ni(itsq)₂,³⁰ by protonation. In the first protonation process, the stabilization of LUMO in **1b** (4.03 eV) is comparable to that in *trans*-Ni(itsq)₂ (4.07 eV) as shown in Figure 3a. However, the stabilization in **1b** is more pronounced compared with that in **1a** (3.95 eV). It is most likely that the different stabilization energy between **1a** and **1b** is related to the character of the Pt–S bond on the opposite side of the protonated nitrogen. Namely, the natural bond orbital (NBO) analysis revealed that the Pt ion has a greater contribution to the Pt–S antibonding orbital in **1b** (75.19%) compared with that in **1a** (65.28%), which leads to a stronger impact of the protonation on the LUMO largely confined to a benzene ring on the opposite side (Figure 3a). As well, the isomerization [i.e., **1b**

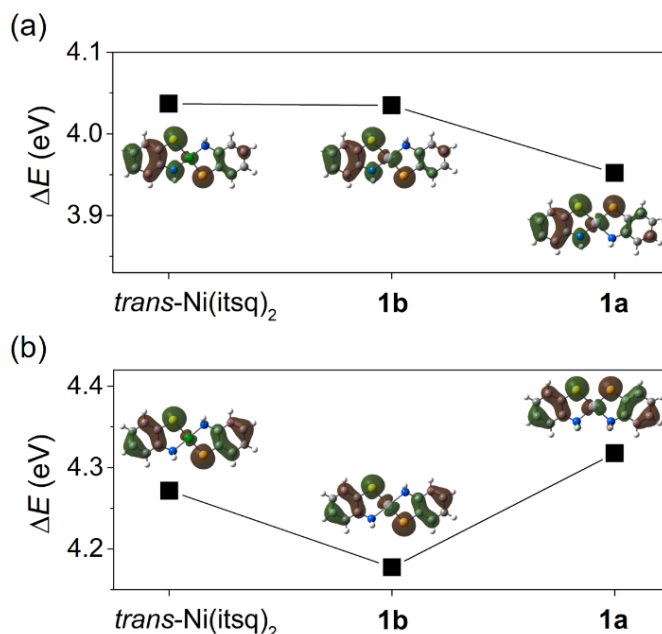
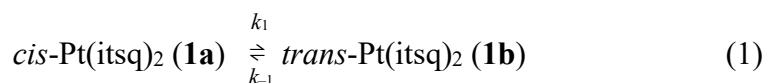


Figure 3. Stabilization of LUMO (ΔE) in *trans*-Ni(itsq)₂ (left), **1b** (middle), and **1a** (right) in the first (a) and second (b) protonation processes. Electron density distributions of LUMO in the monoprotinated (a) and diprotinated (b) states in the three metal complexes are also shown. All calculations were performed using the RB3LYP level of theory.

(4.18 eV) to **1a** (4.32 eV)] can change the stabilization energy of LUMO in the second protonation process greater than the metal substitution [i.e., **1b** (4.18 eV) to *trans*-Ni(itsq)₂ (4.27 eV)] (Figure 3b). This could also be a reflection of the higher contribution of Pt to the Pt–S antibonding orbital in **1a** (65.05%) compared with that in **1b** (62.03%) in a diprotonated state. These results strongly suggest that the change in the geometrical configuration in metal complexes has a drastic effect on proton–electron coupling compared to the metal substitution.

One of the most striking features of *cis/trans* isomers is the isomeric transformation between them, which can be induced by external stimuli such as heat, pressure, light irradiation, and solvent change.^{31–33} In this study, the time-dependent ¹H NMR spectra in organic solvents with various solvent parameters (Table S2^{48,49}) were monitored, to investigate the *cis/trans* isomeric transformation in **1a/1b**. Figure 4a demonstrates the temporal variation of ¹H NMR signals of *cis* (**1a**) and *trans* (**1b**) isomers in chloroform (CDCl₃) at 298 K. To date, the reason that the *cis* isomer was present at the initial stage is not clear. However, the powder X-ray diffraction (PXRD) pattern of the solid obtained by evaporating the solvent immediately after dissolving pure **1b** contained the characteristic reflections of **1a** (Figure S8). While the signal of **1a** steadily diminished within ca. 10 days, the intensity of the signal of **1b** gradually increases until the equilibrium (equation 1) was reached, as in Pt(dbitsq)₂ (dbitsq¹⁻ = 2,4-di-*t*-butyl-6-iminothiosemiquinonate) with bulky *t*-butyl groups.⁵⁰ Similar behavior was observed in the pyridine (C₅D₅N), dichloromethane (CD₂Cl₂), and acetonitrile (CD₃CN) solutions (Figure S9), although the time to reach the equilibrium state was different. PXRD measurements affirmed that the species in the equilibrium state, which was isolated by evaporation of the solvents, is **1b** (Figure S10); namely, the *trans* isomer is the thermodynamically favored form in these solvents.⁵¹



$$\begin{aligned}
[\mathbf{1a}]_t &= [\mathbf{1a}]_0 - \frac{(k_1[\mathbf{1a}]_0 - k_{-1}[\mathbf{1b}]_0)(1 - e^{-(k_1 + k_{-1})t})}{k_1 + k_{-1}} \\
[\mathbf{1b}]_t &= [\mathbf{1b}]_0 + \frac{(k_1[\mathbf{1a}]_0 - k_{-1}[\mathbf{1b}]_0)(1 - e^{-(k_1 + k_{-1})t})}{k_1 + k_{-1}}
\end{aligned}
\tag{2}$$

Figures 4b-4e show the time dependence of the molar ratio of **1a** and **1b** estimated from the intensity ratio of ^1H NMR signals in the four solvents. The transformation could be adequately fitted with conventional equations for a single reversible reaction (equation 2), where the

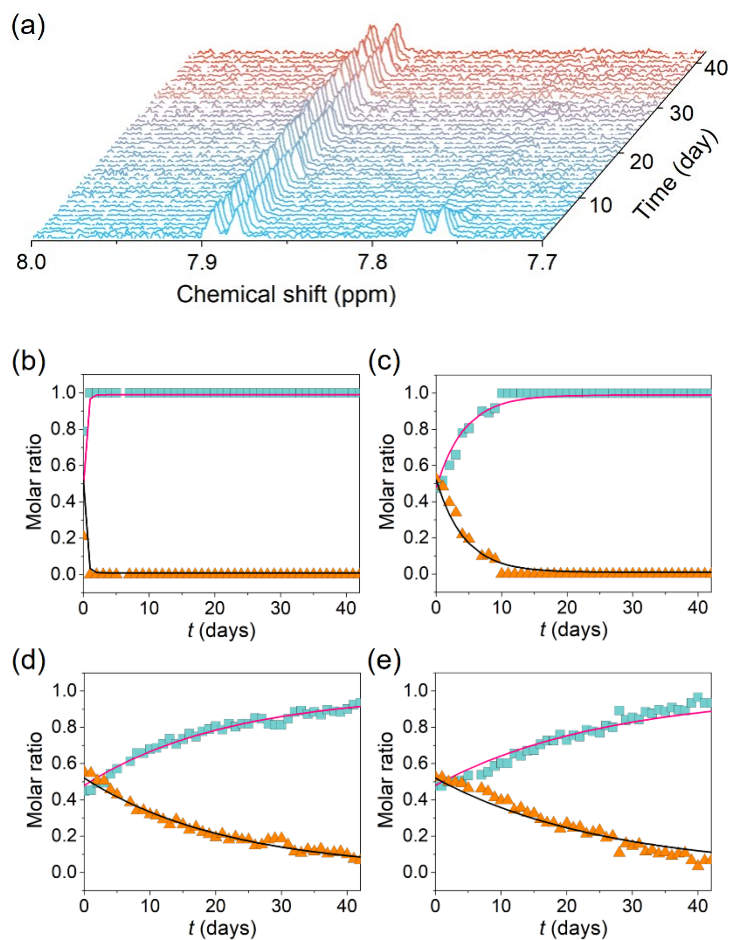


Figure 4. (a) Temporal variation of ^1H NMR signals of **1a** ($\delta \sim 7.77$ ppm) and **1b** ($\delta \sim 7.88$ ppm) in CDCl_3 at 298 K. Time-dependent molar ratio of **1a** (orange triangle) and **1b** (blue square) estimated from the ^1H NMR signal intensity in (b) $\text{C}_5\text{D}_5\text{N}$, (c) CDCl_3 , (d) CD_2Cl_2 , and (e) CD_3CN solutions at 298 K. The black and purple lines are the best fits to equation 2.

equilibrium constant ($K = k_1/k_{-1}$) was assumed to be 100 (i.e., standard Gibbs free energy change $\Delta G^0 = -11.4 \text{ kJ mol}^{-1}$). It turned out that the transformation in $\text{C}_5\text{D}_5\text{N}$ ($k_1 = 3.47 \times 10^{-5} \text{ s}^{-1}$, $k_{-1} = 3.47 \times 10^{-7} \text{ s}^{-1}$) is faster than those in other three solvents ($k_1 = 2.66 \times 10^{-6} \text{ s}^{-1}$ for CDCl_3 , $k_1 = 5.21 \times 10^{-7} \text{ s}^{-1}$ for CD_2Cl_2 , and $k_1 = 4.40 \times 10^{-7} \text{ s}^{-1}$ for CD_3CN). The faster transformation seems to be a consequence of the higher Lewis basicity of pyridine (Gutmann donor number: 33.1⁴⁸), which stabilizes the intermediate state.^{52,53} It is likely that the moderate rate constant in chloroform correlates with its low polarizability ($\pi^* = 0.58$ ⁴⁹), because it is known that the polar solvent favors the formation of the polar *cis* isomer.^{52,53}

To investigate the isomeric transformation from the theoretical viewpoint, the potential energy curve (PEC) for the isomerization was calculated at the B3LYP level of theory in the gas phase.⁵⁴

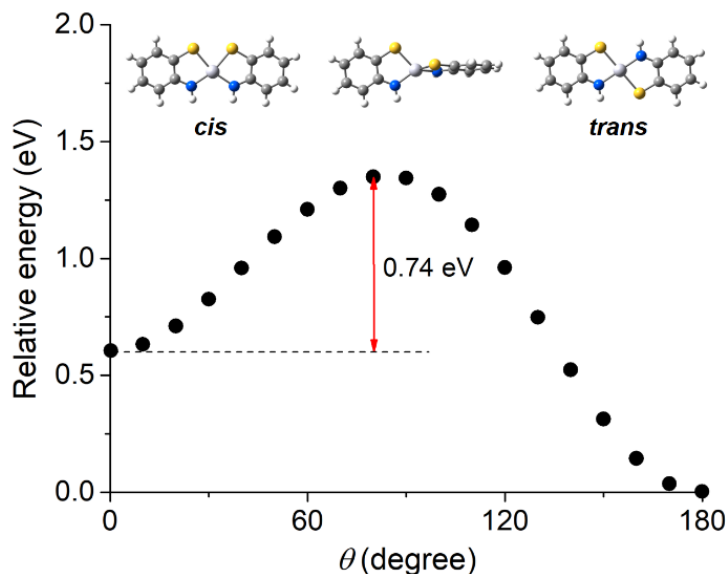


Figure 5. Potential energy curve (PEC) for isomerization along the dihedral angle (θ) between the two ligand planes from 0° (i.e., *cis* form) to 180° (i.e., *trans* form) in $\text{Pt}(\text{itsq})_2$. The relative energy is taken relative to the energy of the *trans* form. Computed geometries of the *cis*, *trans*, and intermediate forms are shown in the top part (gray, C; white, H; blue, N; yellow, S; silver, Pt). All results were calculated at the RB3LYP level of theory.

Figure 5 shows the PEC as a function of the dihedral angle (θ) between the two ligand planes from 0 ° (i.e., *cis* form) to 180 ° (i.e., *trans* form). The DFT calculations predicted that the *trans* form ($E = -40502.07$ eV) is 0.6 eV lower in energy than the *cis* form ($E = -40501.47$ eV), which is consistent with the time-dependent ^1H NMR studies. The curve has a round maximum at $\theta = 80^\circ$, and the energy barrier for the **1a** to **1b** transformation was estimated to be 0.74 eV. Such an energy barrier that separates the two bistable states will provide avenues for exploring the switching of proton–electron coupling by external stimuli. Studies along these lines are in progress.

CONCLUSIONS

In this study, the metal–ligand isomerization between the *cis* and *trans* forms with different proton–electron coupling was investigated in a π -planar platinum complex by combining the experimental and theoretical approaches for the first time. Time-dependent ^1H NMR spectra demonstrated the kinetic transformation from *cis* to *trans* isomers, in which the transformation rate depends largely on the solvent. Theoretical calculations revealed that the isomeric change in the ligands while keeping the components has a greater effect on proton–electron coupling compared to the metal substitution while retaining the geometrical structure of the ligands. We believe that the present study will provide an alternative approach to implementing significant proton–electron coupling in metal complexes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <http://pubs.acs.org>.

Synthetic procedures, measurements details, crystallographic data, band structures, solvent parameters, IR, UV-vis-NIR, CV, ^1H NMR, and PXRD patterns (PDF).

AUTHOR INFORMATION

Corresponding Authors

Yukihiro Yoshida: Division of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan; Email: yoshiday@ssc.kuchem.kyoto-u.ac.jp

Hiroshi Kitagawa: Division of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan; Email: kitagawa@kuchem.kyoto-u.ac.jp

Authors

Pingping Huang: Division of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa-Oiwakecho, Sakyo-ku, Kyoto 606-8502, Japan

Tokutaro Komatsu: School of Medicine, Nihon University, 30-1 Oyaguchi-Kamicho, Itabashi-ku, Tokyo 173-8610, Japan

Yuiga Nakamura: Japan Synchrotron Radiation Research Institute (JASRI), SPring-8, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

Kunihisa Sugimoto: Japan Synchrotron Radiation Research Institute (JASRI), SPring-8, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

Author Contributions

Y.Y. and H.K. conceived and designed the project. P.H. carried out the synthesis, characterization, and other experimental works and analyzed the data. T.K. carried out the band structure calculations. Y.N. and K.S. provided support in single-crystal X-ray diffraction measurements. P.H. and Y.Y. wrote the manuscript with feedback provided by H.K. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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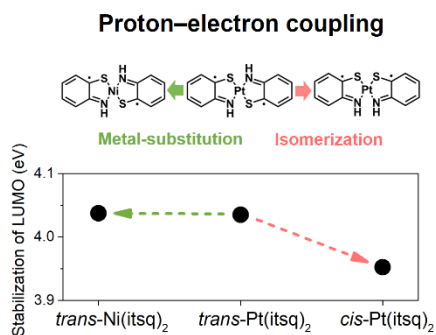
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Table of Contents



Metal–ligand isomerization between the *cis* and *trans* forms with different proton–electron coupling properties was experimentally observed in a π -planar platinum complex in organic solvents. Theoretical calculations revealed that isomerization while keeping the components unchanged has a greater effect on proton–electron coupling compared to the component substitution.