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## (Citation)

Inorganic Chemistry, 60(16):12386-12391

## (Issue Date)

2021-08-16

## (Resource Type)

journal article

## (Version)

Accepted Manuscript

## (Rights)

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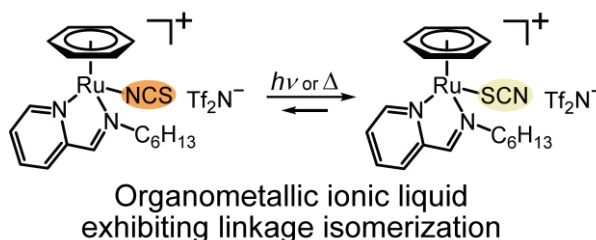
# Photoinduced and Thermal Linkage Isomerizations of an Organometallic Ionic Liquid Containing a Half-Sandwich Ruthenium Thiocyanate Complex

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**ABSTRACT:** Metal complexes with thiocyanate (SCN<sup>-</sup>) ligands typically exhibit *S*- or *N*-coordinated linkage isomers. In this study, to explore ionic liquids that exhibit stimuli-



responsiveness based on linkage isomerization, we synthesized an ionic liquid containing a cationic half-sandwich thiocyanate complex, [Ru(C<sub>6</sub>H<sub>6</sub>)(NCS)L]Tf<sub>2</sub>N<sup>-</sup> (L = *N*-hexyl-2-pyridinemethanimine, Tf<sub>2</sub>N<sup>-</sup> = bis(trifluoromethanesulfonyl)amide anion). The as-synthesized ionic liquid was a 0.7:0.3 mixture of *N*- and *S*-coordinated isomers, presenting as an extremely viscous liquid exhibiting a glass transition at 0 °C. Isomerization from the *N*- to the *S*-coordinated isomer occurred upon UV photoirradiation or heating, although thermal isomerization was accompanied by significant decomposition. The *N*- and *S*-coordinated isomers were separated into brown and orange liquids, respectively, using gel-permeation chromatography. Each isomer exhibited a small

solvatochromic absorption shift in organic solvents, with different solvent dependences observed for the two isomers.

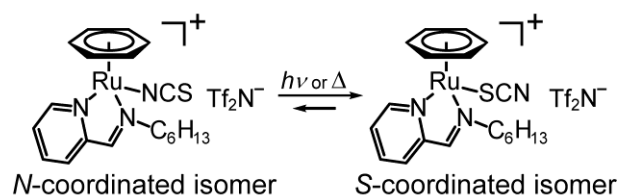
## INTRODUCTION

Ionic liquids, which are salts with melting points below 100 °C, exhibit versatile properties including low volatility, flame retardancy, and high ionic conductivity, with physical properties that may be tuned via component modification.<sup>1</sup> Therefore, extensive research on ionic liquids has been conducted in numerous fields, such as electrochemistry and organic synthesis. Ionic liquids are typically onium salts, although various functional ionic liquids containing metal complexes have been synthesized in recent years.<sup>2-7</sup> Our laboratory has synthesized several ionic liquids containing cationic sandwich or half-sandwich complexes,<sup>8-10</sup> which exhibit unique functionalities such as magnetism, chemical reactivity, and stimuli responsiveness in addition to ionic conductivity.<sup>11-14</sup>

Linkage isomerization is a typical reaction of metal complexes with ambidentate ligands.<sup>15</sup> *S*- and *N*-coordinated isomers exist for metal complexes bearing a thiocyanate (SCN<sup>-</sup>) ligand, and several studies have investigated their linkage isomerizations.<sup>15-25</sup> Noteworthy examples include vapor-induced solid-state isomerization, which enables colorimetric vapor detection,<sup>21,22</sup> and photoisomerization associated with a spin transition.<sup>23</sup> Although such studies focus mainly on simple polypyridyl complexes, some half-sandwich thiocyanate compounds also exhibit linkage isomerization.<sup>24-26</sup> We hypothesized that the isomerization mechanism may be useful for developing novel stimuli-responsive organometallic ionic liquids.

In this study, an ionic liquid containing a cationic half-sandwich Ru thiocyanate complex, [Ru(C<sub>6</sub>H<sub>6</sub>)(NCS)L]Tf<sub>2</sub>N (L = *N*-hexyl-2-pyridinemethanimine, Tf<sub>2</sub>N = bis(trifluoromethanesulfonyl)amide anion, (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>), was synthesized ([**1**]Tf<sub>2</sub>N, **Figure 1**).

The ligand with the hexyl group and the Tf<sub>2</sub>N anion was used to lower the melting point, and the ionic liquid was obtained as a mixture of *N*- and *S*-coordinated isomers. This paper reports the thermal properties, viscosity, and photoinduced and thermal isomerization of the synthesized ionic liquid. In addition, the solvatochromic behavior of each isomer was examined. Although photoisomerization of Ru complexes with ambidentate ligands such as NO has been well documented,<sup>27-30</sup> there seems to be no example of the photoisomerization in Ru–SCN complexes.



**Figure 1.** Linkage isomers of the half-sandwich complex [1]Tf<sub>2</sub>N synthesized in this study.

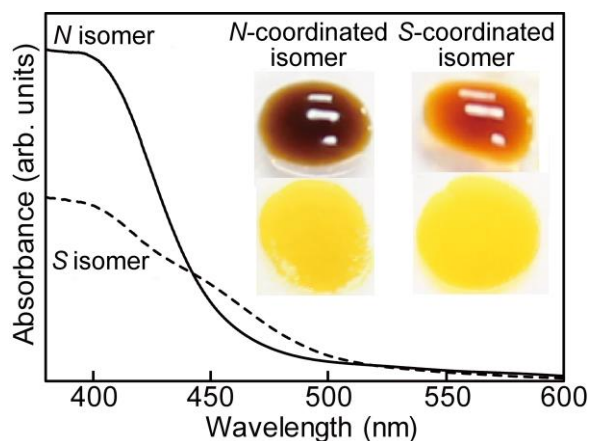
## RESULTS AND DISCUSSION

**Preparation and Properties.** [1]Tf<sub>2</sub>N, obtained as a 0.7:0.3 mixture of *N*- and *S*-coordinated isomers, was an extremely viscous, sticky liquid.

The precursor [1]PF<sub>6</sub> was obtained as a light green powder by the reaction of [RuCl(C<sub>6</sub>H<sub>6</sub>)L]PF<sub>6</sub>, AgPF<sub>6</sub>, and KSCN at ambient temperature (81% yield). The powder was a 0.7:0.3 mixture of *N*- and *S*-coordinated isomers, as determined by <sup>1</sup>H NMR spectroscopy (**Figure S1**, Supporting Information). This salt was an amorphous solid at ambient temperature. [1]Tf<sub>2</sub>N was obtained as a dark brown liquid by the reaction of [1]PF<sub>6</sub> with KTf<sub>2</sub>N (86% yield). The isomer ratio was unchanged by anion exchange. The dominant *N*-coordinated isomer is the kinetic product in acetone, whereas the *S*-coordinated isomer is more thermodynamically stable, as shown below.

The isomers of [1]Tf<sub>2</sub>N were separated using gel permeation chromatography. The droplets of the *N*- and *S*-coordinated liquids were brown and orange, respectively, whereas the liquid films

sandwiched between quartz plates appeared dark and light yellow, respectively. Photographs and UV–vis spectra of the isomers are shown in **Figure 2**. The spectrum of the *N*-coordinated isomer shows a broad peak at approximately 400 nm, whereas that of the *S*-coordinated isomer exhibits small shoulders at approximately 450 nm. The greater absorbance of the former in the visible region is consistent with its darker color. In the IR spectra, the CN stretching vibration peaks for the *N*- and *S*-coordinated isomers were observed at 2096 and 2109  $\text{cm}^{-1}$ , respectively (**Figure S2**, Supporting Information). This is consistent with the data for the half-sandwich complex  $[\text{Ru}(p\text{-cymene})(\text{bpy})(\text{SCN})]\text{PF}_6$  ( $\text{bpy} = 2,2'$ -bipyridine), with the corresponding peaks observed at 2099 and 2109  $\text{cm}^{-1}$ , respectively.<sup>26</sup> **[1]Tf<sub>2</sub>N** (0.7:0.3 mixture of *N*- and *S*-coordinated isomers) was mainly used for the measurements described below owing to the scarcity of the separated samples.



**Figure 2.** UV–vis spectra of the *N*-coordinated (—) and *S*-coordinated (---) isomers of **[1]Tf<sub>2</sub>N**. Photographs of the isomers are shown in the inset: droplets on quartz plates (upper) and films sandwiched between quartz plates (lower).

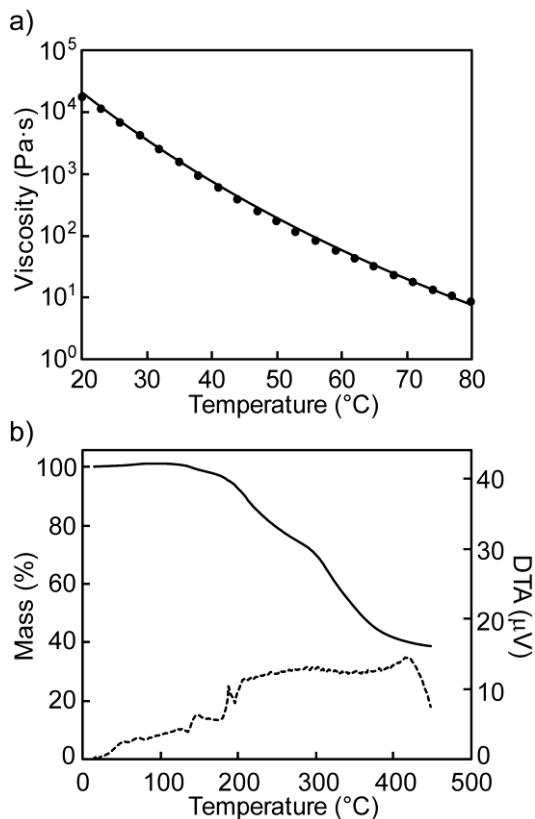
**Viscosity and Thermal Properties.** **[1]Tf<sub>2</sub>N** exhibited an extremely high viscosity, with a glass transition at 0 °C, and underwent thermal decomposition when heated above 125 °C.

The viscosity of [1]Tf<sub>2</sub>N measured between 20 and 80 °C is shown in **Figure 3a** (filled circles). The liquid exhibited extremely high viscosities of 7900 and 7.6 Pa s at 25 and 80 °C, respectively, which are three to five orders of magnitude higher than those of common ionic liquids (*c.f.* [Emim]Tf<sub>2</sub>N:  $4.0 \times 10^{-2}$  and  $8.0 \times 10^{-3}$  Pa s at 25 and 80 °C, respectively<sup>31</sup>). The temperature dependence of viscosity was fitted to the Vogel–Fulcher–Tammann (VFT) equation,  $\eta = \eta_0 \exp(DT_0/(T - T_0))^{32}$  (**Figure 3a**), where  $\eta_0$ ,  $T_0$ , and  $D$  are the viscosity at infinite temperature, the ideal glass transition temperature, and a measure of the fragility of the glass, respectively. The obtained parameters were  $\eta_0 = 1.4(0.7) \times 10^{-6}$  Pa·s,  $T_0 = 158(3)$  K, and  $D = 22(1)$  (standard deviations in parentheses). Thermal decomposition did not occur during the measurements.

Differential scanning calorimetry (DSC) showed that [1]Tf<sub>2</sub>N displays a glass transition at 0 °C and no crystallization at low temperatures. The high glass transition temperature was consistent with the extremely high viscosity at ambient temperature. We also performed DSC analysis of the precursor, [1]PF<sub>6</sub>. This amorphous solid exhibited a glass transition at 60 °C, above which it became a liquid. The DSC thermograms are shown in **Figure S3** (Supporting Information).

The thermal stability of the liquid was examined using thermogravimetric–differential thermal analysis (TG-DTA). The liquid was much less thermally robust than typical onium ionic liquids. The TGA thermogram of [1]Tf<sub>2</sub>N measured at a heating rate of 3 °C min<sup>-1</sup> is shown in **Figure 3b**. The onset of mass loss was observed at approximately 125 °C, and the temperature at which 3 wt% mass loss occurred was 162 °C. Mass loss occurred in three steps, with corresponding changes observed in the DTA thermogram. In the first step, a small mass loss (9 wt%) occurred in the range 130–200 °C, likely corresponding to the dissociation of the benzene ring (calc. 11 wt%). Thermal dissociation of benzene was also observed when the sample was heated in solution. The second and third mass loss steps occurred at 200–300 °C (20 wt%) and above, respectively. [1]PF<sub>6</sub>

displayed a similar TGA thermogram (**Figure S4**, Supporting Information), indicating that the successive decomposition of the cation accounted for the mass losses observed for both salts.



**Figure 3.** (a) Temperature dependence of the viscosity of [1]Tf<sub>2</sub>N (shear rate 1 s<sup>-1</sup>). The curves are fitted using the VFT equation. (b) TG (—) and DTA (---) thermograms of [1]Tf<sub>2</sub>N (3 °C min<sup>-1</sup> under N<sub>2</sub>).

**Photoisomerization.** [1]Tf<sub>2</sub>N exhibited photoisomerization from the *N*- to the *S*-coordinated isomer, which was an equilibrium reaction.

Upon UV photoirradiation of [1]Tf<sub>2</sub>N sandwiched between quartz plates for 90 min (365 nm, LED light), the ratio of the *N*- and *S*-coordinated isomers was changed from 7:3 to 0.45:0.55, and the amount of *S*-coordinated isomer exceeded that of the *N*-coordinated isomer. No distinct color changes were observed upon isomerization. The photoisomerization of the isolated *N*-coordinated

isomer was monitored via IR spectroscopy (**Figure S5**, Supporting Information). The spectra showed a shift in the CN stretching peak in accordance with isomerization. To examine the reversibility of photoisomerization, the photoisomerization of the isolated *S*-coordinated isomer was also investigated; after 90 min of photoirradiation, the ratio of the *N*-coordinated and *S*-coordinated isomers was changed from 0:1 to 0.24:0.76. The presence of the *N*-coordinated isomer indicates the occurrence of a reverse reaction, demonstrating that isomerization is an equilibrium reaction. Photoisomerization was accompanied by slight decomposition (4%), and the liquid became darker in color in this case. The decomposition appeared to be of thermal origin (see below), because an increase in the LED power increased the decomposition with only a slight change in the isomer ratio. To determine whether the isomerization affected the physical properties, the viscosity of [1]Tf<sub>2</sub>N was measured before and after photoirradiation, with no changes observed.

Several Co(III) and Pt(II) thiocyanate complexes are known to exhibit photoisomerization in solution.<sup>20–23</sup> The complexes typically isomerize to their kinetically stable forms in aprotic solvents.<sup>21</sup> The current photoisomerization result suggests that the *S*-coordinated isomer may be kinetically favored in the ionic liquid state, although the *N*-coordinated isomer was the kinetic product in acetone. Furthermore, it was found that the photoirradiation of [1]Tf<sub>2</sub>N in solution was ineffective for inducing isomerization; an acetonitrile coordinated complex [Ru(CH<sub>3</sub>CN)<sub>3</sub>(NCS)L]<sup>+</sup> was formed in acetonitrile, whereas only unidentifiable products were formed in methanol and CH<sub>2</sub>Cl<sub>2</sub>.

**Thermal Isomerization.** Thermal isomerization from the *N*- to the *S*-coordinated isomer was observed in [1]Tf<sub>2</sub>N at elevated temperatures. The isomerization direction was the same as that of photoisomerization, but the reaction was accompanied by severe decomposition.



After heating [1]Tf<sub>2</sub>N at 80 °C for 4 h, the ratio of the *N*- and *S*-coordinated isomers was reversed from 0.7:0.3 to 0.35:0.65. This result indicates that the *S*-coordinated isomer is more thermodynamically stable than the *N*-coordinated isomer. Density functional theory (DFT) calculations revealed that the *S*-coordinated isomer is 4.2 kJ mol<sup>-1</sup> more stable than the *N*-coordinated isomer, which is consistent with the experimental result (**Figure S6**, Supporting Information). However, thermal isomerization was accompanied by severe decomposition (~50%). This decomposition occurred upon the thermal release of benzene from the cation, which yielded a decomposition product insoluble in chloroform. At higher temperatures, the ratio of the *S*-coordinated isomer was increased further, but the decomposition was increased, whereas isomerization did not occur at ambient temperature. The details thereof are provided in the experimental section. Furthermore, the thermal isomerization of the isolated *S*-coordinated isomer was examined. After 4 h of heating at 80 °C, the ratio of the *N*- and *S*-coordinated isomers changed from 0:1 to 0.13:0.87, accompanied by decomposition. This result demonstrates the occurrence of a reverse reaction, and this indicates that thermal isomerization is an equilibrium reaction.

The relative stabilities of the isomers of thiocyanate complexes depend on the complex and are also affected by the solvent.<sup>15</sup> For [Ru(*p*-cymene)(bpy)(SCN)]<sup>+</sup>,<sup>26</sup> an equilibrium isomer mixture is gradually reached upon heating in solution; the *N*-coordinated isomer is favored in acetone, whereas the *S*-coordinated isomer is favored in MeOH. We examined the thermal isomerization of [1]Tf<sub>2</sub>N in solution, but only decomposition was observed in MeOH and dimethyl sulfoxide (DMSO). In chloroform, the ratio of the *S*-coordinated isomer was increased, similar to the neat reaction, accompanied by decomposition.

Ionic liquids with thermally controllable isomerization can be used to record thermal histories. Unfortunately, the synthesized ionic liquid was not sufficiently thermally robust for this purpose.

However, this feature may be improved by molecular modification, considering the superior thermal stability of  $[\text{Ru}(p\text{-cymene})(\text{bpy})(\text{SCN})]^+$ .<sup>26</sup>

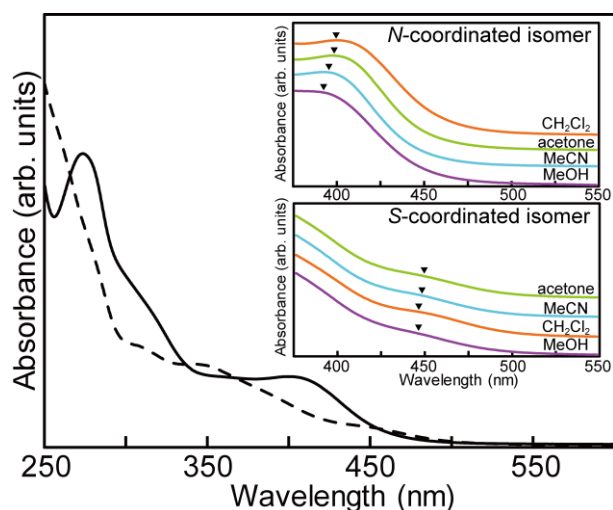
**Solvatochromic Behavior.** The UV–vis spectra of the [1]Tf<sub>2</sub>N isomers were measured in organic solvents. The isomers exhibited solvatochromic absorption shifts with different solvent dependences, although the shifts were slight and not visually distinguishable.

The solutions of each isomer in CH<sub>2</sub>Cl<sub>2</sub>, MeCN, acetone, and MeOH were all yellow in color. The spectrum of the *N*-coordinated isomer shows a peak at approximately 400 nm (**Figure 4**), which exhibits a small solvatochromic shift (**Figure 4**, upper inset). The  $\lambda_{\text{max}}$  in each solvent decreased in the following order: CH<sub>2</sub>Cl<sub>2</sub> (400 nm) > acetone (397 nm) > MeCN (394 nm) > MeOH (391 nm). On the other hand, the *S*-coordinated isomer exhibited a much smaller shift with a different solvent dependence. The spectrum displays a shoulder at approximately 450 nm (**Figure 4**, lower inset), which is blue-shifted in the following order: acetone (450 nm) > MeCN (448 nm) > CH<sub>2</sub>Cl<sub>2</sub> (445 nm) = MeOH (445 nm).

The trend of the solvatochromic shift for the *N*-coordinated isomer was consistent with the solvent polarities  $E^T_N$  (CH<sub>2</sub>Cl<sub>2</sub>: 0.31, acetone: 0.35, MeCN: 0.46, MeOH: 0.76).<sup>33</sup> TD-DFT calculations predicted a UV–vis transition at 399 nm, from HOMO-1 (mixed Ru-SCN orbital) to LUMO (Ru-L orbital). This charge-transfer character accounts for the observed solvent dependence.<sup>34–37</sup> In contrast, the trend of the *S*-coordinated isomer was consistent with the acceptor number  $AN$  (acetone: 12.5, MeCN: 18.9, CH<sub>2</sub>Cl<sub>2</sub>: 20.4, MeOH: 41.5),<sup>38</sup> which reflects the hydrogen bonding abilities of the solvents. The correlation with  $AN$  has also been reported for the solvatochromism of Ru-pyridyl complexes with cyanide ligands.<sup>39</sup> This correlation is reasonable because the terminal N of the SCN<sup>-</sup> ligand can form hydrogen bonds with the solvent. TD-DFT

calculations predicted low-energy transitions (HOMO to LUMO+1) at 457 and 454 nm for the *S*-bonded isomer and its hydrogen-bonded MeOH adduct, respectively, which was consistent with the observed trend.

Several Ru-SCN complexes exhibit solvatochromic behaviors,<sup>34–37</sup> although no such comparative studies on their linkage isomers have been reported. Although the observed solvatochromic differences were very small, the mechanisms underlying them may be useful for controlling the solvatochromic and vapochromic behaviors of ionic liquids.



**Figure 4.** UV-vis spectra of the *N*-coordinated (—) and *S*-coordinated (---) isomers in CH<sub>2</sub>Cl<sub>2</sub> (80 μmol L<sup>-1</sup>). Their spectra in CH<sub>2</sub>Cl<sub>2</sub> (orange), acetone (green), MeCN (pale blue), and MeOH (purple) are shown in the inset. The triangles indicate the peak positions derived from the fourth-order derivatives of the spectra.

## CONCLUSION

An ionic liquid containing a half-sandwich Ru complex bearing a thiocyanate ligand was synthesized, yielding a mixture of *N*- and *S*-coordinated isomers in a 7:3 ratio. Photoinduced and

thermal isomerization from the *N*- to the *S*-coordinated isomer was observed, but heating was accompanied by significant decomposition. The isomers exhibited different solvatochromic absorption shifts in organic solvents. Although the solvatochromic shifts were small in the current complex, the underlying mechanism thereof may be useful for controlling the chromic behavior of ionic liquids via external stimuli.

## EXPERIMENTAL SECTION

**General.**  $[\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2]_2$  and *N*-hexyl-2-pyridinemethanimine (L) were prepared according to literature procedures.<sup>40,41</sup> Other reagents were purchased from Tokyo Chemical Industry. Preparative gel permeation liquid chromatography was performed using an LC-908 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent:  $\text{CH}_2\text{Cl}_2$ , flow rate:  $10 \text{ mL min}^{-1}$ ).  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were recorded using an Avance 400 spectrometer (Bruker). FT-IR spectra were measured using a Nicolet iS5 FT-IR spectrometer (Thermo Fisher Scientific) equipped with an attenuated total reflectance (ATR) unit (diamond). Electrospray ionization-mass spectrometry was conducted using an LTQ Orbitrap Discovery (Thermo Fisher Scientific). DSC was performed using a Q100 differential scanning calorimeter (TA Instruments) at a ramp rate of  $10 \text{ }^\circ\text{C min}^{-1}$  in an aluminum hermetic pan. UV-vis spectroscopy was performed using a V-570 UV-VIS/NIR spectrophotometer (JASCO, Inc.). The samples were placed on quartz plates for the measurements. TG-DTA was performed using a TG8120 thermal analyzer (Rigaku) at a scan rate of 3 or  $10 \text{ }^\circ\text{C min}^{-1}$  under a  $\text{N}_2$  atmosphere. The viscosity was measured using a Discovery HR-2 instrument (TA Instruments). TD-DFT calculations were performed using Spartan'20 software (Wavefunction, Inc.) at the  $\omega\text{B97-D/LanL2DZ}$  level.

**Synthesis of [RuCl(C<sub>6</sub>H<sub>6</sub>)L]PF<sub>6</sub>.** Under an N<sub>2</sub> atmosphere, a solution of [Ru(C<sub>6</sub>H<sub>6</sub>)Cl<sub>2</sub>]<sub>2</sub> (250 mg, 0.50 mmol) and L (194 mg, 1.02 mmol) in MeOH (10 mL) was stirred at ambient temperature for 2 h, as the color of the solution changed from red to dark brown. NH<sub>4</sub>PF<sub>6</sub> (371 mg, 2.28 mmol) was then added to the solution, and stirring was continued for 1 h. The precipitated yellow powder was collected by vacuum filtration. The addition of diethyl ether to the filtrate and subsequent cooling to -4 °C yielded an additional batch, which was collected by filtration and dried under vacuum (499 mg, 91% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 0.90 (t, 3H, CH<sub>3</sub>, J = 6.94 Hz), 1.31–1.44 (br, 6H, CH<sub>2</sub>), 1.96–2.03 (br, 2H, CH<sub>2</sub>), 4.33 (quin, 1H, CH<sub>2</sub>, J = 7.37 Hz), 4.48 (quin, 1H, CH<sub>2</sub>, J = 7.12 Hz), 5.97 (s, 6H, arene), 7.61 (s, 1H, CH, J = 7.30 Hz), 7.91 (d, 1H, CH, J = 7.76 Hz), 8.04 (t, 1H, CH, J = 7.74 Hz), 8.25 (s, 1H, CH), 9.22 (d, 1H, CH, J = 5.56 Hz). FT-IR (ATR, cm<sup>-1</sup>): 556 (P–F), 770, 829 (P–F), 1163, 1240, 1306, 1438, 1480, 1597, 2359, 2858, 2939, 3081. ESI-MS: *m/z* calcd. for C<sub>18</sub>H<sub>24</sub>ClN<sub>2</sub>Ru<sup>+</sup>: 405.0666. Found: 405.0660.

**Synthesis of [Ru(C<sub>6</sub>H<sub>6</sub>)(NCS)L]PF<sub>6</sub> ([1]PF<sub>6</sub>).** AgPF<sub>6</sub> (208 mg, 0.82 mmol) was added to an acetone solution (6 mL) of [RuCl(C<sub>6</sub>H<sub>6</sub>)L]PF<sub>6</sub> (298 mg, 0.54 mmol), and the mixture was stirred at ambient temperature for 60 h. AgCl was then removed by filtration. The complete reaction of [RuCl(C<sub>6</sub>H<sub>6</sub>)L]PF<sub>6</sub> was confirmed by <sup>1</sup>H NMR spectroscopy. KSCN (269 mg, 2.77 mmol) was subsequently added to the filtrate, and the mixture was stirred for 3 h. After solvent evaporation, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 mL), an aqueous solution (15 mL) of NH<sub>4</sub>PF<sub>6</sub> (236 mg, 1.45 mmol) was added, and the resulting mixture was stirred vigorously. The organic layer was separated, washed twice with water (15 mL), and dried over anhydrous MgSO<sub>4</sub>. After solvent removal, diethyl ether was added to the remaining powder and the dispersion was sonicated to remove ether-soluble impurities. The product was collected by filtration as a light green powder

(250 mg, yield 81%). The product was a mixture of *N*- and *S*-coordinated isomers in a 0.7:0.3 ratio.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) for *N*-bound isomer:  $\delta = 0.93$  (m, 3H,  $\text{CH}_3$ ), 1.35–1.40 (br, 6H,  $\text{CH}_2$ ), 2.28–2.37 (m, 2H,  $\text{CH}_2$ ), 4.24–4.31 (br, 2H,  $\text{CH}_2$ ), 6.04 (s, 6H, arene), 7.68 (m, 1H,  $\text{CH}$ ), 7.95–8.16 (m, 2H,  $\text{CH}$ ), 8.36 (s, 1H,  $\text{CH}$ ), 9.07 (d, 1H,  $\text{CH}$ ,  $J = 10.16$  Hz). *S*-bound isomer:  $\delta = 0.93$  (m, 3H,  $\text{CH}_3$ ), 1.35–1.40 (br, 6H,  $\text{CH}_2$ ), 2.28–2.37 (m, 2H,  $\text{CH}_2$ ), 4.24–4.31 (br, 2H,  $\text{CH}_2$ ), 6.02 (s, 6H, arene), 7.68 (m, 1H,  $\text{CH}$ ), 7.95–8.16 (m, 2H,  $\text{CH}$ ), 8.31 (s, 1H,  $\text{CH}$ ), 9.16 (d, 1H,  $\text{CH}$ ,  $J = 10.16$  Hz). ESI-MS:  $m/z$  calcd. for  $\text{C}_{19}\text{H}_{24}\text{N}_3\text{RuS}^+$ : 428.0734. Found: 428.0747. Anal. Calcd. for  $\text{C}_{19}\text{H}_{24}\text{F}_6\text{N}_3\text{PRuS}$ : C, 39.79; H, 4.22; N, 7.33. Found: C, 39.90; H, 4.27; N, 7.22.

**Synthesis of  $[\text{Ru}(\text{C}_6\text{H}_6)(\text{NCS})\text{L}]\text{Tf}_2\text{N}$  ( $[\mathbf{1}]\text{Tf}_2\text{N}$ ).** An aqueous solution (5 mL) of  $\text{KTf}_2\text{N}$  (316 mg, 0.99 mmol) was added to a  $\text{CH}_2\text{Cl}_2$  solution (5 mL) of  $[\mathbf{1}]\text{PF}_6$  (183 mg, 0.33 mmol), and the mixture was stirred vigorously for 30 min at ambient temperature. The organic layer was collected, and the anion-exchange procedure was repeated thrice. The organic layer was dried over anhydrous  $\text{MgSO}_4$  and filtered, before the solvent was removed using a rotary evaporator. The absence of  $\text{PF}_6^-$  was confirmed by  $^{19}\text{F}$  NMR spectroscopy. The product was dried under vacuum at 40 °C overnight, yielding the desired dark brown liquid (203 mg, 86% yield). This liquid was a mixture of *N*- and *S*-coordinated isomers in a 0.7:0.3 ratio. Small quantities of the *N*- and *S*-coordinated isomers were separated using gel permeation chromatography (eluent: chloroform, flow rate 10  $\text{mL min}^{-1}$ ). The retention times were 20.8 and 20.4 min, respectively.  $^1\text{H}$  NMR (400 MHz, DMSO) *N*-bound isomer:  $\delta = 0.88$  (m, 3H,  $\text{CH}_3$ ), 1.34 (s, 6H,  $\text{CH}_2$ ), 1.75–1.80 (m, 1H,  $\text{CH}_2$ ), 1.93–1.97 (m, 1H,  $\text{CH}_2$ ), 4.19–4.26 (m, 1H,  $\text{CH}_2$ ), 4.58–4.64 (m, 1H,  $\text{CH}_2$ ), 6.24 (s, 6H, arene), 7.89 (m, 1H,  $\text{CH}$ ), 8.24 (t, 1H,  $\text{CH}$ ,  $J = 6.98$  Hz), 8.33 (t, 1H,  $\text{CH}$ ,  $J = 8.36$  Hz), 8.87 (s, 1H,  $\text{CH}$ ), 9.62 (d, 1H,  $\text{CH}$ ,  $J = 5.28$  Hz). *S*-bound isomer:  $\delta = 0.88$  (m, 3H,  $\text{CH}_3$ ), 1.34 (s, 6H,  $\text{CH}_2$ ), 1.75–1.80 (m, 1H,  $\text{CH}_2$ ),

1.93–21.97 (m, 1H,  $CH_2$ ), 4.28–4.34 (m, 1H,  $CH_2$ ), 4.38–4.45 (m, 1H,  $CH_2$ ), 6.23 (s, 6H, arene), 7.81 (m, 1H,  $CH$ ), 8.24 (t, 1H,  $CH$ ,  $J = 6.98$  Hz), 8.33 (t, 1H,  $CH$ ,  $J = 8.36$  Hz), 8.89 (s, 1H,  $CH$ ), 9.43 (d, 1H,  $CH$ ,  $J = 5.52$  Hz). FT-IR (ATR,  $cm^{-1}$ ): 528, 739, 770, 788, 839, 1226, 1347, 1439, 1480, 1599, 2099 (CN), 2859, 2931, 3085. ESI-MS:  $m/z$  calcd. for  $C_{19}H_{24}N_3RuS^+$ : 428.0734. Found: 428.0746. Anal. Calcd. for  $C_{19}H_{24}F_6N_3PRuS$ : C, 35.61; H, 3.42; N, 7.91. Found: C, 36.17; H, 3.45; N, 7.62.

**Photoinduced and thermal isomerizations of [1]Tf<sub>2</sub>N.** Photoisomerization was performed with the samples sandwiched between quartz plates using an LC-L1V3 Lightningcure UV-LED lamp (365 nm, 180 mW  $cm^{-2}$ , Hamamatsu Photonics) as the light source. The sample was placed on a cooling plate set at 10 °C during photoirradiation. Upon photoirradiation, the *N*-isomer:*S*-isomer ratio of [1]Tf<sub>2</sub>N was changed from 0.7:0.3 to 0.45:0.55 over 90 min. In the <sup>1</sup>H NMR spectrum of the product, free benzene (4%) was observed at 7.3 ppm; this was released through decomposition. Photoirradiation with more intense light increased the decomposition, indicating that the generated heat caused decomposition. The reaction rates also depended on the sample thickness, because each isomer showed absorption at 365 nm. In addition, photoirradiation of the solutions of [1]Tf<sub>2</sub>N in dichloromethane-*d*<sub>2</sub>, chloroform-*d*<sub>3</sub>, acetonitrile-*d*<sub>3</sub>, and methanol-*d*<sub>4</sub> was performed. The product in acetonitrile-*d*<sub>3</sub> was identified as [Ru(CD<sub>3</sub>CN)<sub>3</sub>(SCN)L]<sup>+</sup> from the <sup>1</sup>H NMR and HRMS spectra, whereas the other solvents yielded only unidentifiable products.

The thermal isomerization was examined as follows. Under a N<sub>2</sub> atmosphere, [1]Tf<sub>2</sub>N (19 mg, 0.026 mmol) was heated at 80 °C for 4 h. After cooling to ambient temperature, the sample was dissolved in chloroform (10 mL), and the insoluble decomposition product was removed by filtration. The solvent was removed from the filtrate under reduced pressure, and the residue was

dried under vacuum at 40 °C for 4 h (31 mg, 46% yield). The *N*-isomer:*S*-isomer ratio in the resultant liquid was 0.35:0.65. [1]Tf<sub>2</sub>N isomerization was slower at 70 °C (isomer ratio: 0.43:0.57 at 4 h), although the yield did not improve. Isomerization was faster at 90 °C (isomer ratio: 0.28:0.72 at 4 h), but further decomposition resulted in a very low yield (6%).

The thermal isomerization of [1]Tf<sub>2</sub>N in chloroform-*d* at 50 °C was monitored using <sup>1</sup>H NMR spectroscopy (**Figure S7**, Supporting Information). The ratio of the *S*-coordinated isomer increased with time, and the *N*-isomer:*S*-isomer ratio was changed from 0.7:0.3 to 0.56:0.44 over 6 days. The solution remained yellow, but a small amount of dark brown precipitate gradually formed. In the <sup>1</sup>H NMR spectra, signals representing free benzene gradually appeared, with ratios of 3% and 9% after 1 and 6 days, respectively, relative to the complex. The benzene ligand is released from the complex, yielding the decomposition product. In addition, reactions in other solvents were investigated. [1]Tf<sub>2</sub>N decomposed within a few days in coordinating solvents such as DMSO-*d*<sub>6</sub> and methanol-*d*<sub>4</sub> upon heating at 50 °C, yielding numerous unidentifiable signals in the <sup>1</sup>H NMR spectra.

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## Notes

The author declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was financially supported by KAKENHI (grant number 20H02756) from the Japan Society for the Promotion of Science (JSPS) and a Grant-in-Aid for JSPS Research Fellows (grant number 21J12056).

## Supporting Information

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

<sup>1</sup>H NMR, IR, and UV-vis spectral data, DSC and TG-DTA thermograms, and DFT calculation results (PDF)

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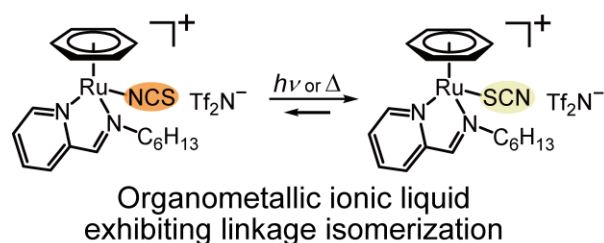
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## Table of Contents



An ionic liquid containing a cationic half-sandwich Ru thiocyanate complex was synthesized. Isomerization from the *N*- to the *S*-coordinated isomer occurred upon UV photoirradiation or heating.

# Supporting Information

## Photoinduced and Thermal Linkage Isomerizations of an Organometallic Ionic Liquid Containing a Half-Sandwich Ruthenium Thiocyanate Complex

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### Contents

**Figure S1.** <sup>1</sup>H NMR spectra of the compounds synthesized in this study.

**Figure S2.** IR spectra of the *N*-coordinated and *S*-coordinated isomers and [1]Tf<sub>2</sub>N.

**Figure S3.** DSC thermograms of [1]Tf<sub>2</sub>N and [1]PF<sub>6</sub>.

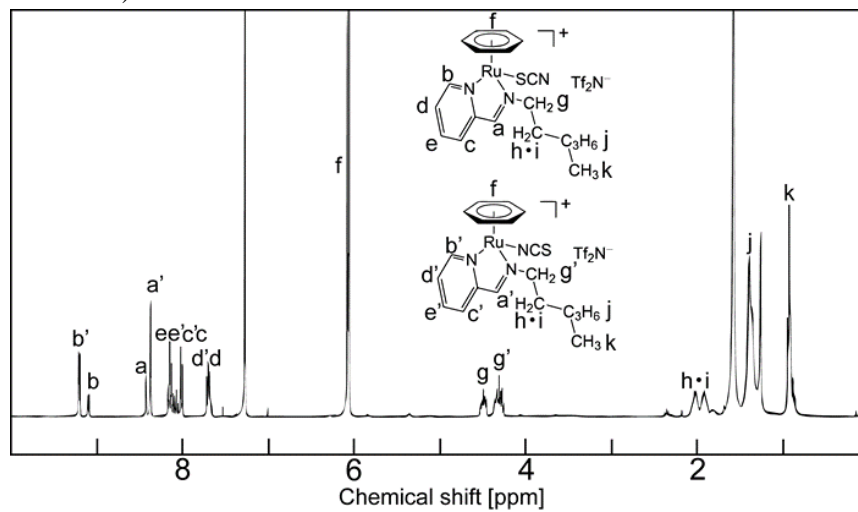
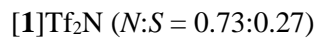
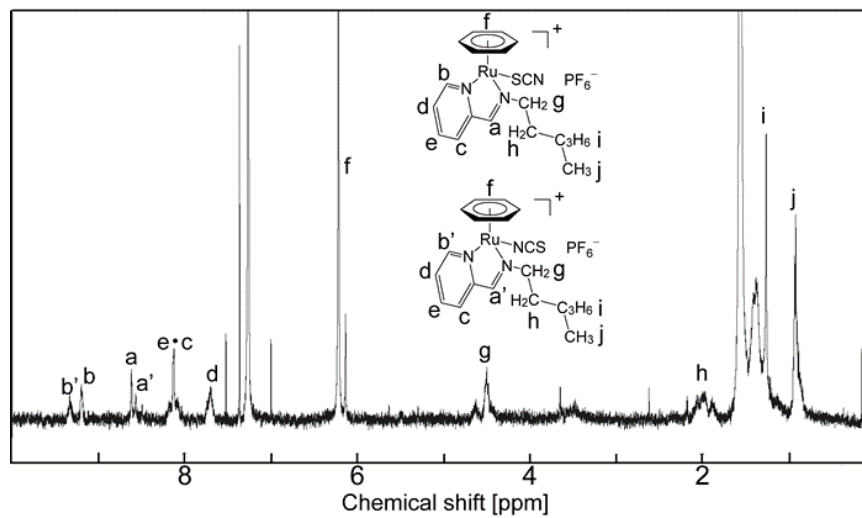
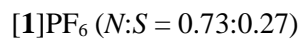
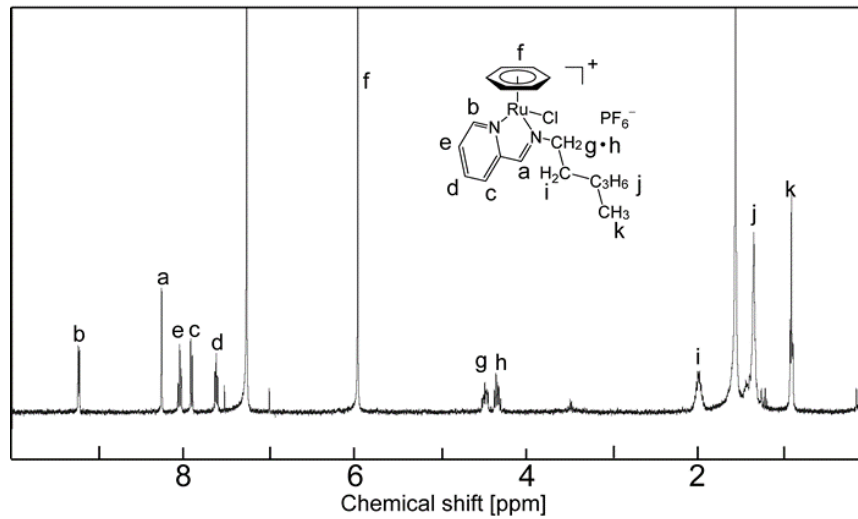
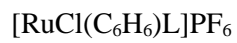
**Figure S4.** TG-DTA thermograms of [1]Tf<sub>2</sub>N and [1]PF<sub>6</sub>.

**Figure S5.** IR spectra of the *N*-coordinated isomer taken upon photoirradiation.

**Figure S6.** Optimized geometries of the *N*- and *S*-coordinated isomers obtained using DFT calculations.

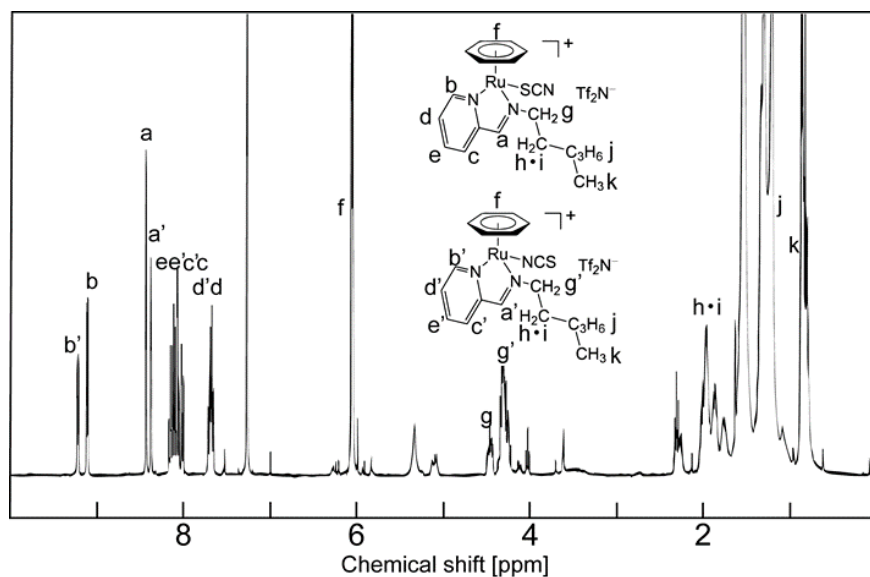
**Figure S7.** <sup>1</sup>H NMR spectra of [1]Tf<sub>2</sub>N (*N*:*S* = 0.73:0.27, CDCl<sub>3</sub> solution) measured before and after heating.

**Figure S8.** UV-Vis spectra and photographs of the *N*-coordinated and *S*-coordinated isomers in dichloromethane and methanol.

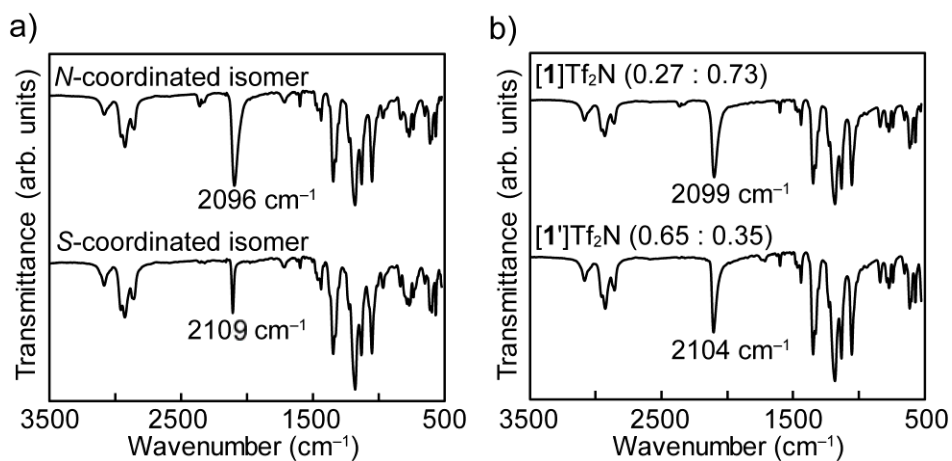




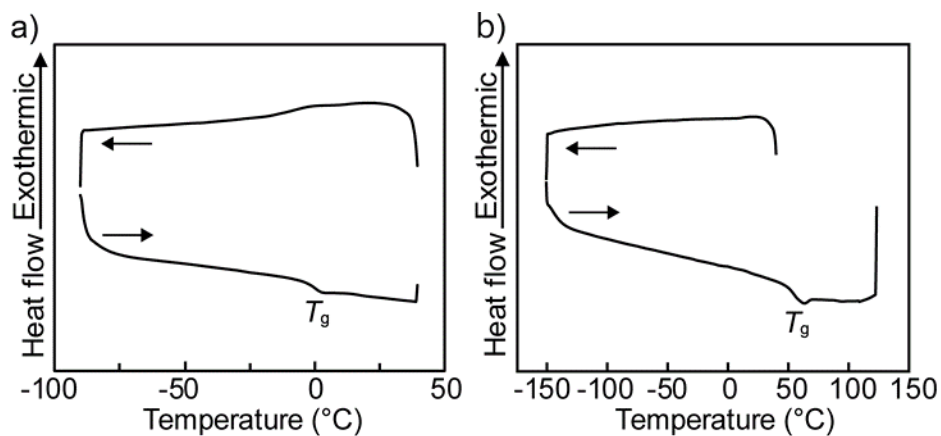
[1']Tf<sub>2</sub>N (after thermal isomerization, *N*:*S* = 0.35:0.65)



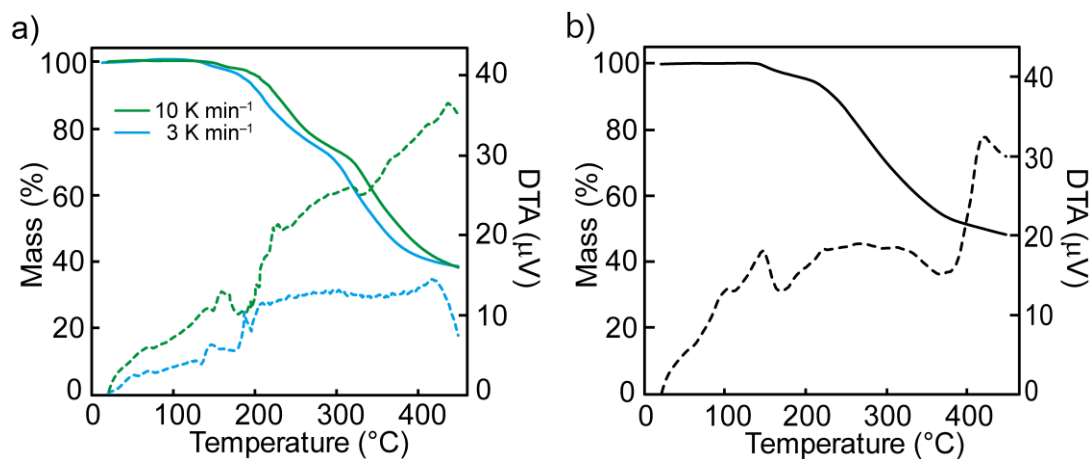
**Figure S1.** <sup>1</sup>H NMR spectra of the compounds synthesized in this study (CDCl<sub>3</sub>).



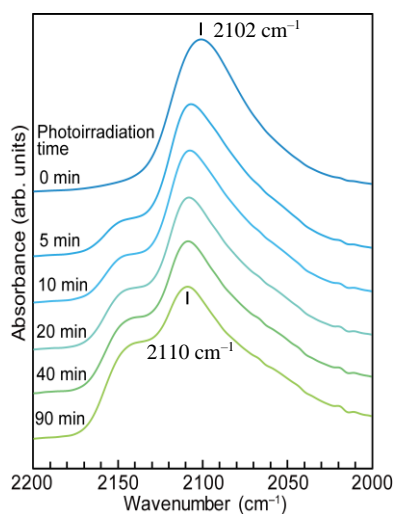
**Figure S2.** IR spectra of (a) the *N*-coordinated and *S*-coordinated isomers and (b) [1]Tf<sub>2</sub>N and [1']Tf<sub>2</sub>N (after thermal isomerization).



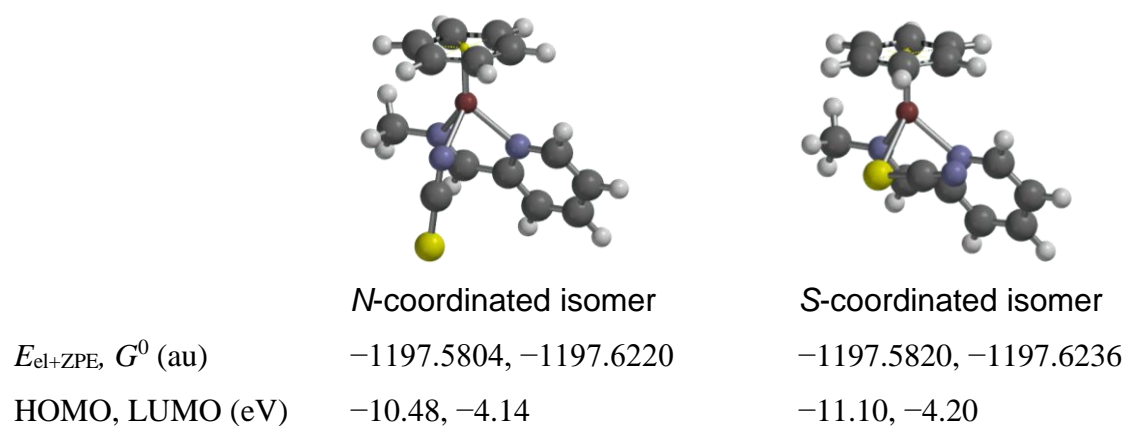
**Figure S3.** DSC thermograms of [1]Tf<sub>2</sub>N (left) and [1]PF<sub>6</sub> (right).



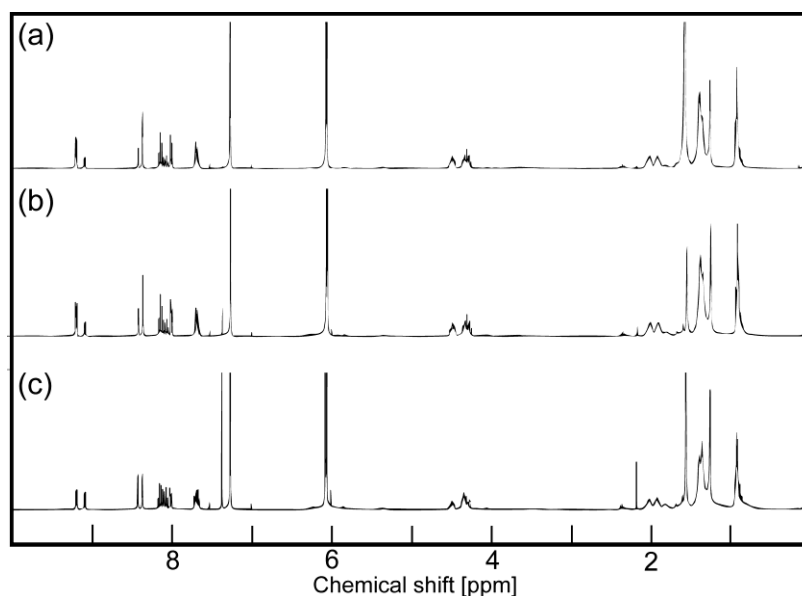
**Figure S4.** TG (—) and DTA (---) thermograms of (a) [1]Tf<sub>2</sub>N (10 and 3 °C min<sup>-1</sup>) and (b) [1]PF<sub>6</sub> (10 °C min<sup>-1</sup>).



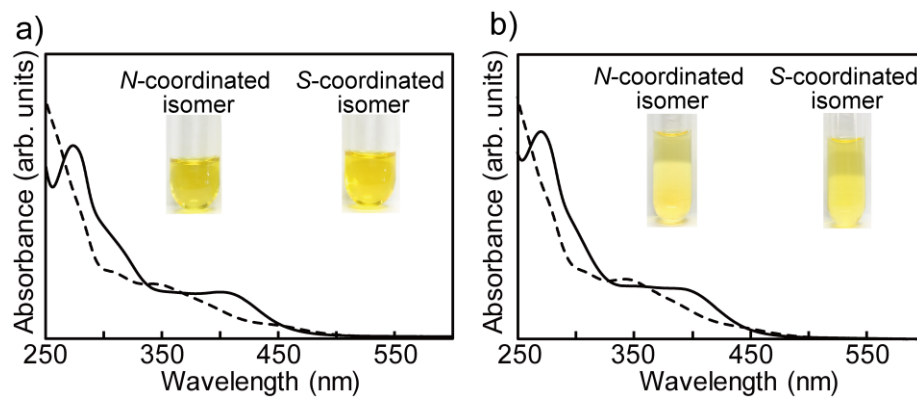
**Figure S5.** IR spectra of the N-coordinated isomer taken upon photoirradiation (KBr plate, transmission spectra).



**Figure S6.** Optimized geometries of the *N*- and *S*-coordinated isomers obtained using DFT calculations. The total energy ( $E_{\text{electronic+ZPE}}$ ), Gibbs energy ( $G^0$ ), and energies of the HOMO/LUMO levels of each isomer are shown below each structure.



**Figure S7.**  $^1\text{H}$  NMR spectra of  $[\mathbf{1}]\text{Tf}_2\text{N}$  ( $N:S = 0.73:0.27$ ,  $\text{CDCl}_3$  solution) (a) Before heating, (b) after 1 day and (c) after 6 days of heating at  $50\text{ }^\circ\text{C}$ .



**Figure S8.** UV-Vis spectra and photographs of the *N*-coordinated (—) and *S*-coordinated (---) isomers in (a) dichloromethane and (b) methanol (concentrations:  $80 \mu\text{mol L}^{-1}$ ).