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Solid-state Thermal and Photochemical *E*/*Z* Isomerization of Bidentate-*N*,*S* Schiff Base Ligands in Iridium(III) Complexes

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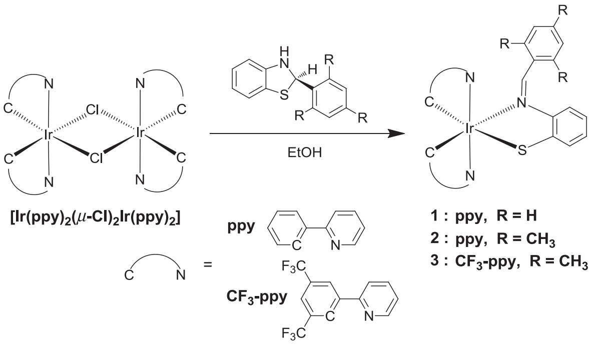
The newly prepared [IrL(ppy or CF_3-ppy$)_2$] complexes with a bidentate-*N*,*S* Schiff base ligand (L) showed thermal and photochemical *E*/*Z* conversions in the solid state, which are tuned by the modification of a pendent phenyl group of L and a phenyl group of ppy.

In recent years, there has been considerable research interest in molecular switches that show interconversion between two different states in response to external stimuli such as heat, light, and electric field.[1,2] One promising molecular switch candidate involves a photochemically promoted *E*/*Z* isomerization of stilbene, azobenzene, and their derivatives, which has received much attention because of the various applications as photoresponsive material.[3–5] While benzylideneanilines (Ar–CH=N–Ar′) also show *E*/*Z* isomerization,[6] their photogenerated *E*- and *Z*-isomers are thermally unstable in general and revert rapidly to their initial isomer state.[7,8] Therefore, no molecular switches have been accomplished by using the *E*/*Z* isomerization of benzylideneanilines to date. Recently, it has been reported that the *E*- and *Z*-isomers of this class of compounds are stabilized by complexation, although reversible isomerization has not been recognized yet.[9,10] Herein we report the synthesis and characterization of a new class of iridium(III) complexes with a bidentate-*N*,*S* Schiff base ligand, [Ir(L^1 or L^2)(ppy or CF_3-ppy$)_2$] (L^1: 2-(benzylideneamino)benzenethiolate, L^2: 2-[(mesitylmethylidene)amino]benzenethiolate, ppy: 2-phenylpyridine, CF_3-ppy: 2-[3,5-bis(trifluoromethyl)phenyl]pyridine), which form both the *E*- and *Z*-isomers for the –CH=N– double bond. Remarkably, [IrL^2(ppy$)_2$] and [IrL^2(CF_3-ppy$)_2$] were found to show the *Z*-to-*E* isomerization by heat and the reverse *E*-to-*Z* isomerization by light in the solid state. To our knowledge, such a reversible *E*/*Z* conversion in the solid state in response to external stimuli is unprecedented.

The reactions of [Ir(ppy$)_2$(μ-Cl$)_2$Ir(ppy$)_2$][11,12] with 2-phenylbenzothiazoline and 2-mesitylbenzothiazoline[13,14] in ethanol gave brown (**1**) and orange (**2**) compounds, respectively (Scheme 1). These compounds were assigned as mononuclear iridium(III) complexes with a Schiff base ligand, [IrL^1(ppy$)_2$] (**1**, L^1: 2-(benzylideneamino)benzenethiolate) and [IrL^2(ppy$)_2$] (**2**, L^2: 2-[(mesitylmethylidene)amino]benzenethiolate), based on UV–vis, IR, and NMR spectroscopies, together with elemental analyses.



Scheme 1. Synthesis of iridium(III) complexes.

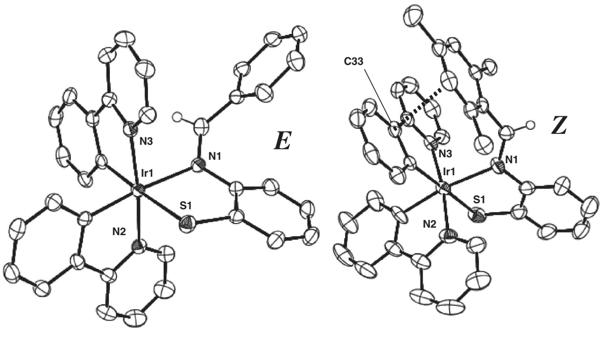


Figure 1. Molecular structures of **1** (left) and **2** (right). Hydrogen atoms, except for an azomethine proton, were omitted for clarity.

The molecular structures of **1** ([IrL^1(ppy$)_2$]) and **2** ([IrL^2(ppy$)_2$]$\cdot$2CH_2Cl_2) were determined by X-ray crystallography.[15] As shown in Figure 1, each of **1** and **2** consists of two bidentate-*C*,*N* ppy ligands and one bidentate-*N*,*S* Schiff base ligand (L^1 or L^2), which chelate to an Ir^{III} center to form a distorted octahedral structure with a trans-N_{ppy} geometry. The bond distances and angles around the Ir^{III} atom in **1** are very similar to those in **2**. The Ir–S bonds in **1** (2.447(2) Å) and **2** (2.4283(15) Å) are relatively long because of the trans influence due to the *C* donor of ppy. The most remarkable structural feature is that **1** and **2** each exists as a single isomeric form, adopting the *E*-geometry for **1** and the *Z*-geometry for **2** (Figure 1). Molecular model examinations revealed that in **1** the *E*-geometry is less sterically crowded than the *Z*. On the other hand, there exists a serious steric repulsion between a methyl group on the pendent phenyl ring and an *N*,*S*-chelating phenyl ring in the *E*-geometry of **2**, which seems to be responsible for the selective isolation of the *Z*-isomer. Thus, the absence/presence of methyl groups on the pendent phenyl ring significantly affects the *E*–*Z* isomerism of this class of complexes. In crystal **2**, the *Z*-geometry appears to be sustained by an intramolecular face-to-face interaction between the pendent phenyl ring of L^2 and the ppy phenyl ring (Figure 1); the separation between C33 and the pendent phenyl ring is 3.242(6) Å and the dihedral angle between the two phenyl rings is 5.3(3)°.

To examine the stability of **1** and **2** in solution, their ^{1}H NMR spectra were measured in DMSO-d_6 at room temperature. Just after the dissolution, the spectrum of **1** gave two sets

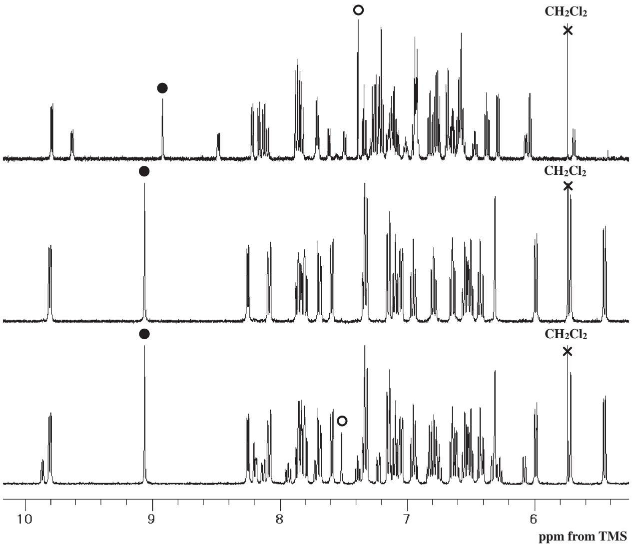


Figure 2. ^{1}H NMR spectra in DMSO-d_6; **1** just after the dissolution (top), **2** just after the dissolution (middle), and **2** after 6 h (bottom) (●; azomethine proton of *Z*-isomer, ○; azomethine proton of *E*-isomer).

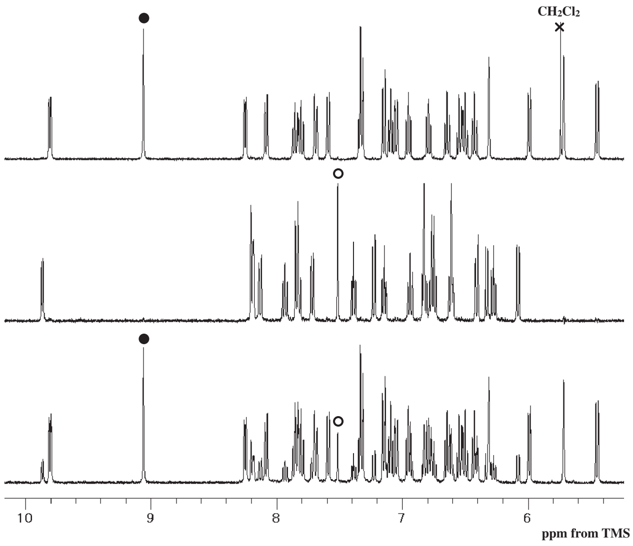


Figure 3. ^{1}H NMR spectra of **2** just after the dissolution in DMSO-d_6; the original sample (top), the sample after heating to 280 °C (middle), and the sample after irradiation for 5 h (bottom) (●; azomethine proton of *Z*-isomer, ○; azomethine proton of *E*-isomer).

of signals, in which two azomethine singlet signals appear at 7.39 and 8.92 ppm (Figure 2).[16] This spectrum remained unchanged at least for 1 day. On the other hand, a single set of signals was observed in the ^{1}H NMR spectrum of **2** just after the dissolution, showing an azomethine singlet at 9.06 ppm (Figure 2). This spectrum gradually changed with time and reached equilibrium after 6 h (Figure S1[17]), which showed two sets of signals including a new azomethine singlet signal at 7.52 ppm in addition to the original azomethine signal at 9.06 ppm (Figure 2). These results imply that **1** and **2** are both converted to a mixture of the *E*- and *Z*-isomers in solution accompanied by the partial *E*-to-*Z* and *Z*-to-*E* isomerizations, respectively, although the conversion for **2** occurs much slower than that for **1**. From the integrations of the characteristic azomethine signals,[18] together with those of the doublet signals due to an aromatic proton of ppy at ca. 10 ppm, **1** and **2** were estimated to contain the *E*- and *Z*-isomers in a ca. 1.6:1 and a 1:3 ratios, respectively, in the equilibrium state in solution.

The thermal stability of **1** and **2** in the solid state was investigated by the measurements of thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC). The TG indicated that **1** and **2** are thermally stable until ≈250 and ≈300 °C, respectively, except for the release of solvated dichloromethane (Figure S3[17]). Of note is the observation of anomalous thermal behavior at ≈250 °C in the DTA and DSC for **2**, while such behavior was not detected for **1** until its decomposition temperature. To clarify the cause of this observation, samples of **2** were heated to 220 °C or to 280 °C, and their ^{1}H NMR spectra were measured just after dissolving in DMSO-d_6. Interestingly, the sample heated to 280 °C ($\mathbf{2_E}$) gave only a set of signals for the *E*-isomer showing an azomethine signal at 7.52 ppm, with the complete disappearance of an original azomethine signal (9.06 ppm) for the *Z*-isomer (Figure 3). On the other hand, the ^{1}H NMR spectrum of the sample heated to 220 °C was the same as that before heating. This implies that the exothermic peak at ≈250 °C observed for **2** is due to the *Z*-to-*E* thermal isomerization. To check the possibility of the reverse *E*-to-*Z* conversion by light, the sample of $\mathbf{2_E}$ obtained by heating was then irradiated with a mercury lamp for 5 h.[19] The ^{1}H NMR spectrum of this irradiated sample showed signals corresponding to both the *E*- and the *Z*-isomers in an *E*:*Z* ratio of ca. 1:3 (Figure 3). Thus, the *E*-isomer of **2** was largely converted to the *Z*-isomer by light in the solid state. It should be noted that **1** did not experience such an *E*/*Z* isomerization by heat and light under the same conditions, which was confirmed by the ^{1}H NMR spectroscopy.

The finding of this unique *E*/*Z* isomerization for **2** prompted us to prepare an analogous iridium(III) complex containing CF$_3$-ppy, in place of ppy, [IrL^2(CF$_3$-ppy)$_2$] (**3**). This complex was successfully synthesized by the reaction of [Ir(CF$_3$-ppy)$_2$-(μ-Cl)$_2$Ir(CF$_3$-ppy)$_2$][20] with 2-mesitylbenzothiazoline in ethanol and was characterized by UV–vis, IR, and NMR spectroscopies, together with elemental analysis. The ^{1}H NMR spectrum of **3** just after dissolving in DMSO-d_6 at room temperature exhibited a single set of signals with an azomethine singlet at 8.98 ppm, indicating the selective formation of the *Z*-isomer (Figure 4). As in the case of **2**, this spectrum gradually changed with time (Figure S2[17]), and two sets of signals involving two azomethine singlet signals at 7.73 and 8.98 ppm with an integration ratio of ca. 1:2 were observed after 6 h. In the DTA and DSC measurements, **3** displayed an exothermic peak at ≈170 °C until its decomposition temperature of ≈330 °C (Figure S3[17]). Thus, samples of **3** were heated to 150 °C or to 190 °C, and their ^{1}H NMR spectra were measured just after dissolving in DMSO-d_6. While the ^{1}H NMR spectrum of the sample heated at 150 °C was the same as that before heating, the sample heated at 190 °C ($\mathbf{3_E}$) showed a different set of signals, in which an azomethine singlet signal appeared at 7.73 ppm with the complete disappearance of an azomethine signal at 8.98 ppm (Figure 4). This indicates that the complete *Z*-to-*E* thermal conversion takes place for **3**, as in the case of **2**, although its conversion

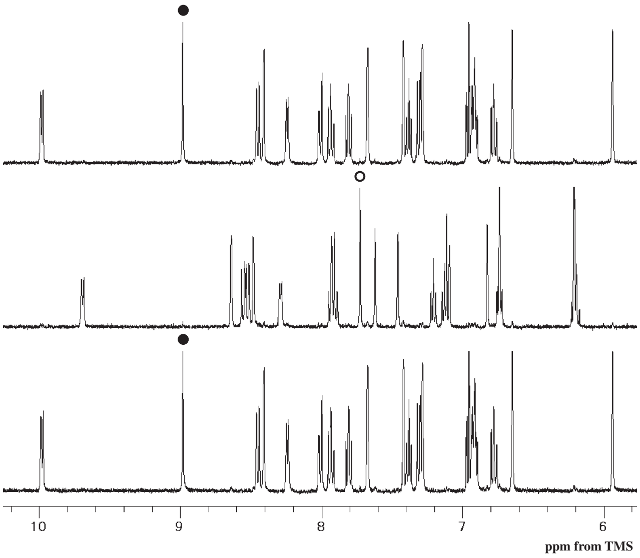


Figure 4. ^{1}H NMR spectra of **3** just after dissolution in DMSO-d_6; the original sample (top), the sample after heating to 190 °C (middle), and the sample after irradiation for 5 h (bottom) (●; azomethine proton of *Z*-isomer, ○; azomethine proton of *E*-isomer).

temperature (≈170 °C) is much lower than that for **2** (≈250 °C). The sample of $\mathbf{3_E}$ obtained by heating was then irradiated with a mercury lamp for 5 h.[19] Remarkably, only a single set of signals corresponding to the original *Z*-isomer was observed in the ^{1}H NMR spectrum of this irradiated sample (Figure 4). Thus, it is seen that the *E*-isomer of **3** is completely converted to the *Z*-isomer by light in the solid state.

In conclusion, we showed that the [IrL(ppy or CF_3-ppy)$_2$] complexes with a bidentate-*N*,*S* Schiff base ligand (L) are isolated as a single *E* or *Z* isomeric form in the solid state, which is converted to a mixture of the *E*- or *Z*-isomers in solution. The selective formation of the *E*- or *Z*-isomer in the solid state, as well as its preferential formation in solution, was found to be markedly affected by the introduction of methyl groups to the pendent phenyl group of L. Notably, this modification of the phenyl group led to the complete *Z*-to-*E* isomerization by heat and the significant *E*-to-*Z* isomerization by light in the solid state. Furthermore, the complete *E*-to-*Z* photochemical isomerization, besides the complete *Z*-to-*E* thermal isomerization, was achieved by the introduction of CF_3 groups to the coligand ppy. Thus, the judicious modification of bidentate-*N*,*S* Schiff base ligands, in combination with the modification of bidentate-*C*,*N* aromatic coligands, makes it possible to produce a molecular switching system that interconverts completely between the *E*- and *Z*-isomers in response to external factors.

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15 Single crystals of **1** and **2** suitable for X-ray analyses were obtained by dissolving their powder samples in dichloromethane/methanol (9:1), followed by storing in a refrigerator. However, all attempts to crystallize **3** failed. *Crystal data*: **1**: $C_{35}H_{26}IrN_3S$, $M_r = 712.85$, $0.30 \times 0.15 \times 0.15\,mm^3$; $T = 200(2)\,K$; monoclinic, $P2_1/n$, $Z = 4$, $a = 9.778(10)$, $b = 21.47(2)$, $c = 13.841(13)\,Å$, $\beta = 108.78(3)°$, $V = 2751(5)\,Å^3$, $\mu = 4.959\,mm^{-1}$, $F(000) = 1400$, $D_{calcd} = 1.721$ g cm^{-3}, $2\theta_{max} = 54.9°$. A total of 44 oscillation images were collected. Of the 26360 reflections collected, 6271 were unique ($R_{int} = 0.0522$). Final $R_1 = 0.0248$ for 4598 reflections with $I > 2\sigma(I)$ (363 parameters) and $wR = 0.0366$ for all reflections. CCDC 782660. **2**: $C_{40}H_{36}Cl_4IrN_3S$, $M_r = 924.78$, $0.30 \times 0.20 \times 0.10\,mm^3$; $T = 200(2)\,K$; triclinic, $P\bar{1}$, $Z = 2$, $a = 9.803(4)$, $b = 12.956(4)$, $c = 15.496(7)\,Å$, $\alpha = 101.024(17)$, $\beta = 92.071(16)$, $\gamma = 105.874(16)°$, $V = 1849.9(12)\,Å^3$, $\mu = 3.988\,mm^{-1}$, $F(000) = 916$, $D_{calcd} = 1.660\,g\,cm^{-3}$, $2\theta_{max} = 55.0°$. A total of 44 oscillation images were collected. Of the 18274 reflections collected, 8409 were unique ($R_{int} = 0.1187$). Final $R_1 = 0.0447$ for 5602 reflections with $I > 2\sigma(I)$ (460 parameters) and $wR = 0.0887$ for all reflections. CCDC 782661.

16 Powder X-ray diffraction study indicated that the bulk sample of **1** used for ^{1}H NMR spectral measurement is identical with the crystal **1** used for single-crystal X-ray analysis.

17 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

18 In the *E*-isomer, the azomethine proton locates in the vicinity of the ppy phenyl ring as found in the crystal structure of **1**, which is responsible for the upfield shift of the azomethine signal for the *E*-isomer relative to that for the *Z*-isomer.

19 Each solid sample was exposed to a mercury lamp without filters.

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