Chemical Stimuli Induced Phosphorescence Modulation of Secondary Thioamide-Based Pincer Platinum Complexes

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Summary: The photochemical properties of pincer platinum complexes bearing secondary thioamide groups have been examined. The presence of the coordinated secondary thioamide linkage in the pincer ligand was found to work as a reactive site upon addition of bases and anions and to result in modulating absorption and emission properties of the complexes.

Cyclometalated platinum(II) complexes represent an important class of complexes, particularly from the point of view of their luminescent properties and catalytic function.^{1–3} The use of phosphorescent complexes as emitters in light-emitting diodes (LEDs) has attracted much attention from researchers in both academic institutions and industry.⁴ Luminescent cycloplatinated complexes are also potential candidates for luminescent sensors, in which the incorporation of various reactive sites into a ligand framework has been examined.^{5,6} We previously reported that κ^3 SCS pincer Pt(II) and Pd(II) complexes containing thioamidebased pincer ligands exhibited strong phosphorescent emission

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Scheme 1. Equilibrium of Secondary Thioamide Group under Neutral and Basic Conditions



in the glassy frozen state and in the solid state.⁷ As an extension of this research, we here demonstrate that the presence of a secondary thioamide group in the pincer ligand framework induces modulating the luminescent properties of the complexes.

The secondary thioamide group is involved in equilibrium with its amino-thione and imino-thiol tautomers, as shown in Scheme 1, and exhibits stronger acidity than the corresponding amide group.⁸ Consequently, the secondary thioamide ligands are easily deprotonated to produce their thionate anionic form, which enhances the electron donor ability of the sulfur atom via the N-to-S backbone. The N–H hydrogen of thioamide also exhibits strong hydrogen bond donor ability, which is discussed in recent reports on anion receptors⁹ and supramolecular networks.¹⁰

This situation motivates us to utilize the secondary thioamide group as not only a coordination site but also a reactive site on the ligand for modulating the photoluminescent properties of the pincer complexes upon exposure to chemical stimuli. We here report that pincer complexes bearing secondary thioamide groups exhibit a luminescent modulation upon the addition of a base and anions. Among the pincer complexes, [2,6-bis(ben-

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Figure 1. Changes in (a) absorption (inset: absorbance change at 450 nm) and (b) emission spectra of $1 (5 \times 10^{-5} \text{ M in THF} \text{ at room temperature})$ upon addition of DBU.

zylaminothiocarbonyl)- $\kappa^2 S_s S'$ -phenyl- κC^1]chloroplatinum(II) (1) was selected for initial investigation because it possessed good solubility in common organic solvents and phosphorescent emission at room temperature; thus, the spectral features of 1 have mainly been examined.

Results and Discussion

Complex 1 was prepared in accordance with the previous reports⁷ and was characterized by NMR and FAB-MS spectroscopy and elemental analysis. Complex 1 has absorption bands in the visible region of 400–500 nm. The absorption bands exhibit negative solvatochromism (Figure S1 in the Supporting Information), which has been often observed for metal-to-ligand charge transfer (MLCT) transitions.¹¹ Complex 1 is light-emitting in solution at room temperature, and the emission has a decay lifetime (τ) of 8.5 μ s in the glassy frozen state (λ_{em} 578 nm), which is indicative of phosphorescent emission. These observations are consistent with those for previously reported pincer Pt(II) complexes.⁷ Related pincer ligands and their Pt(II) complexes (2–4, Chart 1) were prepared and characterized analogously (see the Supporting Information).

The effect of deprotonation of the coordinated pincer ligand on the absorption and emission properties of **1** was examined by adding a small, controlled amount of THF solution containing 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Upon the addition of DBU, the MLCT band at 450 nm gradually decreased with



Figure 2. Changes in (a) absorption and (b) emission spectra of 1 $(5 \times 10^{-5} \text{ M}, \text{ in THF at room temperature})$ upon addition of TBACI.

Chart 1. SCS Pincer Pt(II) Complexes



isosbestic points at 366 and 527 nm that were observed up to a DBU/1 ratio of 1 (as depicted in Figure 1a). When larger amounts of DBU were added, further changes in absorption spectra were observed and the change leveled off at a DBU/1 ratio of about 2 (see also Figure 1a inset), indicating that the deprotonation of the N-H units of 1 consecutively proceeded to give a dideprotonated form of 1, as shown in Scheme 2. After treatment with the base, the addition of an excess of methanesulfonic acid (MSA) to the solution led to the immediate recovery of 1. The reversible deprotonation-protonation behavior of 1 was also monitored by emission spectroscopy. The emission peak at 632 nm gradually decreased in intensity upon the addition of DBU, and the emission almost disappeared upon the addition of 1 equiv of DBU (Figure 1b), indicating that the monodeprotonation of 1 caused the quenching. From a change in emission intensity of **1** with DBU ($pK_a(DBU-H^+) = 19.1$ in THF¹²), pK_{a1} of the secondary thioamide unit of **1** was estimated





Tuble I. Thotophysical Data for Complexes 1								
	1		2		3		4	
		$+Cl^{-a}$		$+Cl^{-a}$		$+ Cl^{-a}$		$+Cl^{-a}$
$\lambda_{abs}^{\ b}/nm \ (\epsilon, \ 10^3 \ M^{-1} \ cm^{-1})$	257 (34.0)	256 (31.9)	254 (29.7)	254 (29.0)	248 (25.4)	245 (23.7)	245 ^c (23.9)	245 ^c (23.9)
	450 (8.7)	431 (9.9)	451 (7.1)	432 (8.2)	448 (5.9)	428 (6.7)	447^{c} (8.1)	447^{c} (8.1)
$\lambda_{\rm em}^{\ b}/\rm{nm}$, room temp	632	608	635	613	630	614		
$\lambda_{\rm em}^{d}/\rm{nm}, 77~\rm{K}$	578	563	583	563	570	562	638	637
$\phi_{\rm em}$, e room temp	0.06	0.12	0.05	0.09	0.03	0.06		
rel $\phi_{\rm em}$, ^f 77 K	0.6	0.7	0.5	0.6	0.3	0.4	0.2^{g}	0.2^{g}
$\tau^{h}/\mu s$, room temp	1.4	2.0	1.4	1.9	0.7	1.5		
τ^i/μ s, 77 K	8.5	10.0	7.4	8.1	4.0	4.4	5.2^{g}	5.6 ^g

Table 1. Photophysical Data for Complexes 1–4

^{*a*} A 600 equiv amount of TBACl was added. ^{*b*} In THF. The values in parentheses are molar absorption coefficients. ^{*c*} In CH₂Cl₂. ^{*d*} In 2-MeTHF glass matrix at 77 K. ^{*e*} Absolute quantum yield in THF at room temperature. ^{*f*} In 2-MeTHF glass matrix, the relative quantum yield values at 77 K were estimated from the ratio of the integrated emission intensity area of each sample to that of *fac*-tris(2-phenylpyridine)iridium as a standard (regarding the quantum yield value as 1.0). ^{14 g} In a CH₂Cl₂–THF (3:2) glass matrix at 77 K. ^{*h*} Emission decay lifetime in 2-MeTHF glass matrix at 77 K.

to be 17.7 (Figure S2 in the Supporting Information). The reversible protonation upon adding MSA to give **1** was confirmed. Similar changes in the absorption and emission spectra of **1** were observed by treatment with other bases such as 1,5-diazabicyclo[4.3.0]nonene (DBN) and *N*,*N*,*N'*,*N'*-tetramethylguanidine (TMG: $pK_a(TMG-H^+) = 17.8$ in THF¹²), whereas the addition of excess Et₃N ($pK_a(Et_3N-H^+) = 14.9$ in THF¹²) did not cause a significant spectral change. The result of ¹H NMR spectroscopy also suggests the deprotonation of **1**. Upon the addition of excess DBU, the N–H proton resonance of **1** completely disappeared in the ¹H NMR spectrum.

In contrast to the optical response of 1 to the bases, we found that the addition of tetra-*n*-butylammonium chloride (TBACl) induced an enhancement of the emission intensity of 1. Figure 2 shows changes in the absorption and emission spectra of 1 upon the addition of TBACl at room temperature. As shown in Figure 2a, the addition of TBACl to the THF solution led to a blue shift of the MLCT absorption band from 450 to 431 nm. The addition of TBACl also caused a blue shift of the emission spectrum by 24 nm with an approximately 2.3-fold increase in emission intensity upon excitation at 441 nm (at which the change in absorbance was minimum; $\Delta_{abs} = \pm 0.01$). The change in the emission spectrum was accompanied by an increase in the luminescence decay lifetime ($\tau = 1.4$ to 2.0 μ s). It is known that the N-H hydrogen of secondary thioamide units exhibits affinity toward anions.⁹ Among the anions (used as a tetra-nbutylammonium (TBA) salt) tested, the most significant emission enhancement of 1 was observed for Cl⁻ ion followed by $Br^- > BF_4^- > PF_6^-$, as depicted in Figure S3 (Supporting Information); this trend reflects the hydrogen bond acceptor ability of the anions.¹³ Similar enhancement of emission properties was also observed upon the addition of tetraphenylphosphonium chloride. The hydrogen-bonding interaction of 1 with Cl⁻ ion was also monitored by ¹H NMR spectroscopy; the addition of excess TBACl led to a downfield shift of the N-H resonance by 0.40 ppm (Figure S4, Supporting Information).

Similar changes in the absorption and emission spectra were observed for the other pincer Pt(II) complexes 2 and 3 bearing secondary thioamide groups. Table 1 summarizes optical data

for the pincer Pt complexes. In contrast to 1-3, 4, a related complex bearing a tertiary thioamide group, was spectroscopically unreactive upon the addition of excess base as well as TBACl and essentially exhibited the same absorption and ¹H NMR spectra. These observations reveal that the formation ofa hydrogen-bonding interaction between the N–H hydrogen of the complexes and Cl⁻ ion is essential to the enhancement of emission properties of the complexes.

These observations suggest that the formation of hydrogen bonds between the N-H hydrogen of 1 and Cl⁻ ion blocks the nonradiative decay channels of the excited state of 1 in solution at room temperature. The interaction of Cl⁻ ion with 1 is considered to remove the ability of the solvent molecules on 1 to quench the ³MLCT emissive state and to result in the increase in τ .¹⁵ Actually, 1 exhibits weak emission in DMSO solution, which acts as both a strong hydrogen bond acceptor and a quencher of the emission of 1;¹⁶ the addition of Cl^{-1} ion to the DMSO solution of 1 also led the enhancement of emission intensity. Alternatively, the hydrogen-bonding interaction of Cl⁻ ion with the N-H hydrogen of 1 may rigidify the molecules in solution, rendering the relaxation of the excited state of 1 to the ground state via nonradiative decay channels less efficient. 6c,d,17 As shown in Table 1, the emission enhancement upon the addition of Cl^- ion is small at 77 K; the complexes 1-3 seem to have an energetically stable conformation and no molecular reorganization is present in the low-temperature glass matrix.¹⁸

As described above, the incorporation of a coordinated secondary thioamide linkage into the pincer ligand framework allows its Pt complex to take part in chemical reactions and hydrogen-bonding interactions and to result in a modulation of its photoluminescent properties. Although the hydrogen-bonding ability of 1 with anions is poor in the present study, the luminescent properties of the pincer ligands bearing secondary thioamide groups are of interest because this will open the way to manipulating luminescent properties of cycloplatinated complexes upon exposure to chemical stimuli.

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Experimental Section

General Procedures. NMR spectra were recorded on a JEOL JNM-EX-400 and JEOL JNM-EX-270 NMR spectrometers. Elemental analyses were carried out with a Yanaco CHN Corder MT-5 instrument. Absorption spectra were recorded using a Shimadzu UV-2550 UV-visible spectrophotometer. The emission spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. To measure the PL characteristics of the complexes in solution and the glass-matrix state, the dissolved oxygen in the solution was removed by bubbling with N₂ for 30 min. Quantum yields at room temperature were measured using an absolute PL quantum yield measurement system (C9920-02, Hamamatsu photonics k.k.). Samples for time-resolved measurements were excited at 337 nm using an N₂ laser, and the luminescence was detected with a photomultiplier tube (Hamamatsu R928) and recorded using a digital storage oscilloscope, before transfer to a PC for analysis.

Synthesis of [2,6-Bis(benzylaminothiocarbonyl)- κ^2 S,5'-phenyl- κC^1]chloroplatinum(II) (1). A mixture of *N*,*N*'-dibenzyl-1,3-benzenedicarbothioamide (376 mg, 1.0 mmol) and K₂PtCl₄ (413 mg, 1.0 mmol) in acetic acid (5 mL) was refluxed for 72 h. The resulting orange precipitate was filtered and washed with methanol and water to give a bright reddish powder (520 mg, 89% yield). FAB-mass: m/z 556 [M - Cl]⁺, 592 [M + H]⁺. ¹H NMR (400 MHz in DMSO-

*d*₆): δ 11.24 (s, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.47–7.31 (m, 11H), 5.00 (s, 2H). ¹³C{¹H} NMR (67 MHz in DMSO-*d*₆): δ 201.40, 162.44, 142.51, 135.52, 128.46, 127.75, 127.55, 127.62, 120.13, 49.55. Anal. Calcd for C₂₂H₁₉ClN₂PtS₂: C, 43.60; H, 3.16; N, 4.62; Cl, 5.85; S, 10.58. Found: C, 43.83; H, 3.22; N, 4.67; Cl, 5.34; S, 10.63.

PL Titration of 1 and pK_a Determination. The pK_{a1} of the secondary thioamide unit of **1** was determined by titrating a solution of **1** with aliquots of a solution of DBU. Details are given in the Supporting Information.

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Supporting Information Available: Text and figures giving details of the syntheses, characterization data, UV—vis absorption spectra, PL spectra, and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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