

Synthesis of Hypervalent Gallium(III) Complexes and Their Ability to Turn-On Luminescent Sensors for Lewis Bases

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Abstract

The introduction of main-group elements into the π -conjugated systems enables the modulation of optical properties based on changes in the coordinated state of the elements, and the use of heavy elements with high Lewis acidity is expected to broaden the range of coordination response. In this study, we focus on hypervalent gallium azobenzene complexes with variable coordination motifs because of a wide accessible space around gallium. The six-, five-, and four-coordinated gallium azobenzene complexes were isolated with pyridine ligands, and we observed that the coordination of pyridine can dynamically change in the solution. Interestingly, the enhancement of the absolute fluorescence quantum yields was observed by the suppressing structural relaxation as increasing the coordination number. Furthermore, it was found that the emission efficiency was enhanced as increasing donor number which represents the strength of Lewis basicity. Finally, we demonstrated that the filter paper soaked by the synthesized gallium complex was prepared, and it worked as a turn-on luminescent sensor to easily visualize strength of Lewis basicity of solvents by simply dropping the solvent on the paper. Our findings are valuable for the development of designable and controllable stimuli-responsive materials focusing on the inherent properties of the main-group elements and π -conjugated systems.

1 Introduction

2 π -Conjugated molecules are versatile platforms for developing organic optoelectronic devices such as organic light
3 emitting diodes (OLEDs)¹ and organic photovoltaics (OPVs)² because of their excellent optical properties and high electrical
4 conductivity derived from their unique electronic states. To induce further functions and tune them for applications, many
5 researchers have devoted much effort to realizing diverse static and dynamic properties by elaborating π -conjugated systems.
6 For example, solvatochromic materials are versatile as an imaging tool with high visibility and high resolution not only for
7 evaluating the environmental factors, such as polarity, but also for monitoring significant but tiny changes in molecular
8 environments.^{3,4} In general, solvatochromic properties can be obtained from donor–acceptor π -conjugated systems.^{5,6} So far,
9 the changes in the optical properties of conventional solvatochromic dyes are crucially dependent on the polarity of solvents,
10 and it is difficult to discriminate the solvents with similar polarity. More recently, a different strategy has been required to
11 classify the type of solvents with different physical parameters. One of other factors is the coordination ability of solvents.
12 Some transition metal complexes show a change in absorbance of the d–d transition band with a structural change caused by
13 the coordination of the solvent to the metal center.⁷ In this system, the changes in absorption properties and subsequently
14 material color represent the coordinating ability of solvents. However, to the best of our knowledge, few examples have been
15 achieved in which the highly visible luminescence properties can reflect the coordination ability of the solvents regardless of
16 polarity.⁸

17 Besides, the incorporation of main-group elements into the π -conjugated framework provides access to π -electron
18 systems followed by their photophysical and electronic properties.⁹ By altering the valence and coordinated state of the
19 element, various functions are expressed from the element-involving conjugated systems. Heavy main-group elements can
20 form higher coordinated states than a four-coordinated state, and the electronic properties of the resulting compounds have
21 been thoroughly studied.^{10,11} We have been also focusing on the O,N,O-type azobenzene tridentate ligands as π -conjugated
22 scaffolds. By making complexes with various heteroelements, these ligands exhibit large light absorption and intense emission
23 properties originating from not only the large orbital overlap between the highest occupied molecular orbital (HOMO) and
24 the lowest unoccupied molecular orbital (LUMO) but also a wide coordination space because of their high structural planarity.
25 In particular, by coordination of the azobenzene ligands with heavy group 14 and 15 elements such as germanium (Ge), tin
26 (Sn), antimony (Sb), and bismuth (Bi), we have found that the compounds had hypervalent states.^{11,12} In particular, it was
27 shown that the optical properties can be drastically changed in response to external stimuli such as vapors and solvents,
28 accompanied by a reversible coordination number change or an oxidation number change.^{13–16} For example, the coordination

of nucleophiles such as dimethylsulfoxide (DMSO) to the azobenzene ligands has been found to be reversible. Moreover, when the coordination number was altered from five to six using monodentate ligands such as propylamine (PA), or from five to seven using a bidentate ligand such as ethylene diamine (EDA), optical properties were drastically varied¹⁴. However, these changes were monotonously observed as bathochromic or hypsochromic shifts of optical bands, and it is not accomplished yet to tune their electronic properties depending on the kinds of nucleophilic ligands. Therefore, we have focused on the central elements as a design approach to gain insight into the coordination response of main-group elements.

Group 13 elements have empty p orbitals, and their electronegativities are low among main-group elements, suggesting strong electronic interactions with Lewis bases and some group 13 elements complexes are used as Lewis acid catalysis.¹⁷ The most representative examples with group 13 elements are a series of boron complexes. Because of planar and rigid structures, a wide variety of luminophores have been developed based on boron-involving π -conjugated systems.^{18,19} In addition, by adding fluoride anion or other Lewis bases such as ammonia, electronic properties can be altered through the coordination at the boron atom.^{20–23} However, similarly to other examples containing hypervalent group 14 elements, only monotonous ON/OFF switch of luminescent properties have been accomplished in the boron-containing π -conjugated systems. Gallium is a heavy group 13 element and is known to exist in hypervalent states with five-, six-, and more coordinated states.^{24–26} Some gallium complexes have been observed to interact with multiple solvent molecules and to change their optical properties depending on the solvent types.^{27–29} From these information, we presumed that they might be responsive to a wide range of nucleophiles. In particular, considering the fact that the previous gallium complexes with the Schiff base ligand have excellent luminescence properties,³⁰ the gallium complexes bearing azobenzene ligands are expected to induce strong luminescence and dramatic changes in optical properties, which may be useful for more accurate identification of molecular environments.

In this study, we synthesized the hypervalent gallium complexes with the azobenzene ligand and monitored changes in their luminescence properties by the coordination at the gallium atom. From a series of experiments, it was found that the multistep coordination with four-, five-, and six-coordinated states can proceed as well as that the luminescence properties are correspondingly enhanced as the coordination increases through the regulation of the degree of the structural relaxation. In particular, we discovered unique stimuli-responsiveness; when solvent molecules are coordinated at the gallium atom, the luminescence properties can be tuned not by the polarity but by the strength of the Lewis basicity of the solvent. Based on these findings, we constructed a paper-type turn-on luminescent sensor that can easily compare the strength of the Lewis basicity of the ligand. These results indicate that the modulation of the structural relaxation by coordination to hypervalent

gallium should be an effective strategy not only to enhance the optical properties of π -conjugated materials but also to induce unique environmental responsiveness that can be applied to evaluate previously unmeasurable environmental factors.

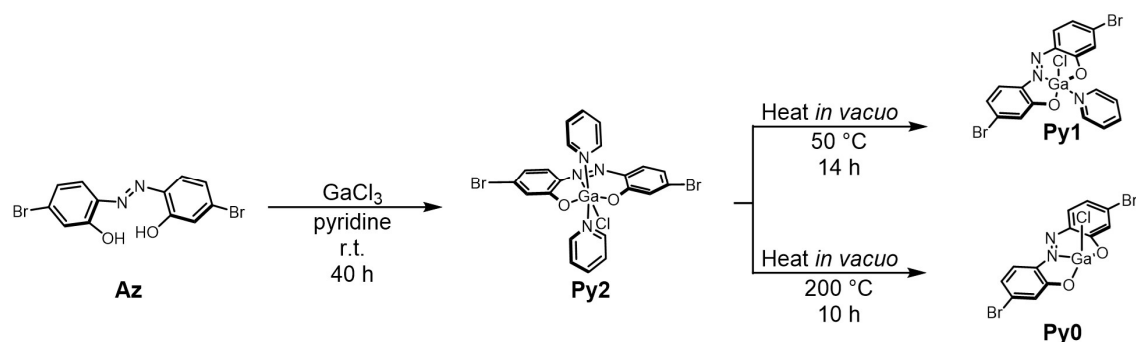
Results and Discussion

Synthesis and Characterization

1. Synthesis

The hypervalent gallium complex **Py2** was synthesized following Scheme 1. The azobenzene tridentate ligand **Az** was prepared according to the literature,³¹ and **Py2** was obtained as a red crystal by the reaction of GaCl₃ with **Az** in the presence of NaH in pyridine in 43% isolated yield. For purification, bromine substituents were introduced to enhance crystallinity. From ¹H NMR measurements, it was suggested that **Py2** formed the six-coordinated state by attaching two pyridine molecules (Chart S1). Interestingly, the five-coordinated hypervalent gallium complex **Py1** and four-coordinated one **Py0** were able to be prepared by stepwise thermal elimination of the pyridine molecules from **Py2**. Figure 1 shows the result of a thermogravimetric analysis (TGA) of **Py2** under N₂ flow. At around 100 °C, the one of coordinating pyridine molecules was eliminated to form **Py1**, and subsequently at around 194 °C, another pyridine molecule was removed, and **Py0** was finally obtained (The weight ratio of pyridine to **Py2** is 12.5%). By optimizing the synthetic methods for **Py1** and **Py0**, we observed that they can be generated by heating **Py2** at 50 °C and 200 °C *in vacuo*, respectively. From the ¹H NMR measurements in CDCl₃, the spectrum of **Py1** was observed, while the spectrum of **Py0** was not able to be obtained directly in a non-coordinating solvent due to its poor solubility. Therefore, the production of **Py0** was identified indirectly by adding 1,10-phenanthroline. As a result, the spectrum of **Py0** including asymmetrical 1,10-phenanthroline were detected without the raw materials **Az** and pyridine (Chart S13). Thus, we concluded that **Py0** should be the pyridine-free gallium complex.

Scheme 1. Synthesis of six- (**Py2**), five- (**Py1**) and four-coordinated (**Py0**) gallium complexes



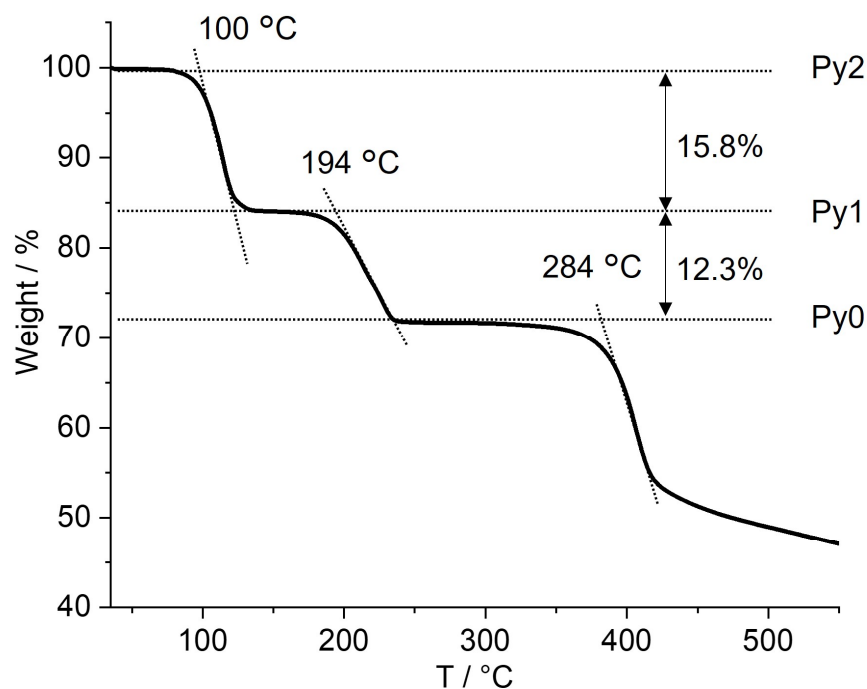


Figure 1. TGA curve of **Py2** from pyrolysis under N₂ atmosphere at a heating rate of 10 °C/min.

2. SC-XRD

Figure 2 shows the ORTEP drawings of **Py1** and **Py2** derivatives obtained from analysis with single crystal X-ray diffraction (SC-XRD). The single crystals of **Py1** and **Py2** were obtained by slow evaporation under N₂ atmosphere in dichloromethane and in pyridine/chloroform solvent, respectively. The detailed crystallographic data are shown in Tables S2 and S3 and Figures S2 and S3. **Py1** forms a five-coordinated state with the pyramidal geometry where the Cl atom is perpendicular to the π -plane, while **Py2** possesses a six-coordinated state with the octahedral geometry where the Cl atom is parallel to the π -plane. It was shown that the single free pyridine molecule was co-crystallized with **Py2**, which should be responsible for the relatively large weight loss during the first degradation step detected in TGA (Figure 1). Next, we focused on the bond length of Ga–N in each complex. In **Py2**, the lengths are 2.10–2.14 Å, and they are an intermediate value between the covalent bond length ($\Sigma r_{\text{cov}}(\text{Ga}, \text{N})$ 1.95 Å) and the sum of van der Waals radii ($\Sigma r_{\text{vdW}}(\text{Ga}, \text{N})$ 3.7 Å).^{32,33} The similar situation was observed in the bond lengths of Ga–O and Ga–Cl. This is the typical feature of six-coordinated octahedral geometry, and therefore, **Py2** can be classified as a hypervalent compound.¹¹ In **Py1**, the four bond lengths of Ga–N and Ga–O at basal positions are also between the covalent bond length and the sum of van der Waals radii, whereas the bond length of Ga–Cl at an apical position is 2.20 Å, which is slightly shorter than the covalent bond length ($\Sigma r_{\text{cov}}(\text{Ga}, \text{Cl})$ 2.23 Å).³⁴ This is

also the typical feature of five-coordinated square pyramidal geometry, and it is indicated that **Py1** can be categorized as a hypervalent compound.³⁵

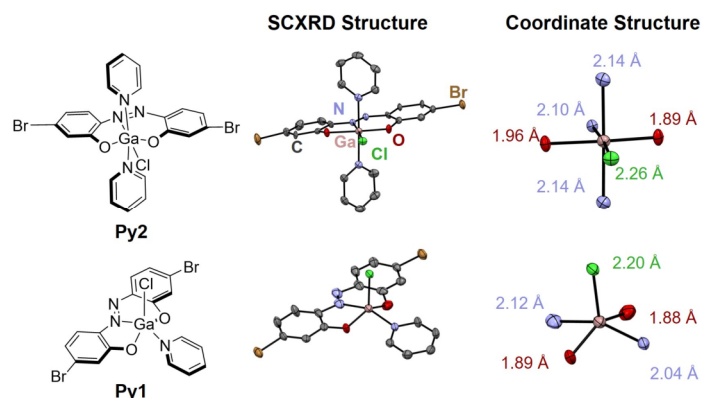


Figure 2. ORTEP drawings of the hypervalent gallium compounds, **Py2** and **Py1** (50% probability for thermal ellipsoids). Hydrogens and disordered atoms are omitted for clarity. The bond lengths of Ga–X (X = N, O, and Cl) are described. All crystallographic data are shown in the Supporting Information.

3. ¹H NMR Spectroscopy

¹H NMR measurements with **Py1** and **Py2** were performed in CDCl₃ as a non-coordinating solvent (Figures 3a and 3b). At room temperature, the ligand moieties (1–3 and 1'–3') were distinguishable in **Py1** and **Py2**, supporting that Ga–N coordination by **Az** should occur in solution. In addition, there is one equivalent of pyridine in **Py1** per the single molecule, whereas there are two and a half equivalents of pyridine per the single molecule in **Py2** including the solvent in the crystal. In **Py2**, despite the fact that there are two and a half pyridine molecules, only the single pyridine was identified from the spectrum, implying that fast exchange at pyridine might occur. In addition, the nuclear Overhauser effect (NOE) measurements showed a correlation between the 1 and 1' protons and a portion of the pyridine (Chart S3). Furthermore, the low-temperature measurement with **Py2** at –60 °C showed a splitting of the peaks from the coordinated pyridine with **Py2** and free pyridine molecules (Figure 3c). When the **Py1** solution was examined at –60 °C, not only **Py1** but also **Py2** spectra were observed, suggesting that **Py1** should be disproportionated at low temperature to **Py0** and **Py2** (Figure 3d). After heating to room temperature again, these signal peaks returned to its initial positions (Charts S5 and S8). These data support that the transformation of **Py1** to other states including **Py0** and **Py2** happens readily. From variable-temperature ¹H NMR spectra, it was confirmed that the peak began to integrate at –30 °C or higher, indicating that the activation energy for the disproportionation of **Py1** to **Py0** and **Py2** is very low. Furthermore, at –40 °C or lower, the peak separated, and the proportion

of **Py2** increased. However, the proportion of **Py2** was still small at $-60\text{ }^{\circ}\text{C}$. From the results of van't Hoff plot, it was revealed that the equilibrium should be significantly biased toward **Py1** (99%) at room temperature (Figure S1).

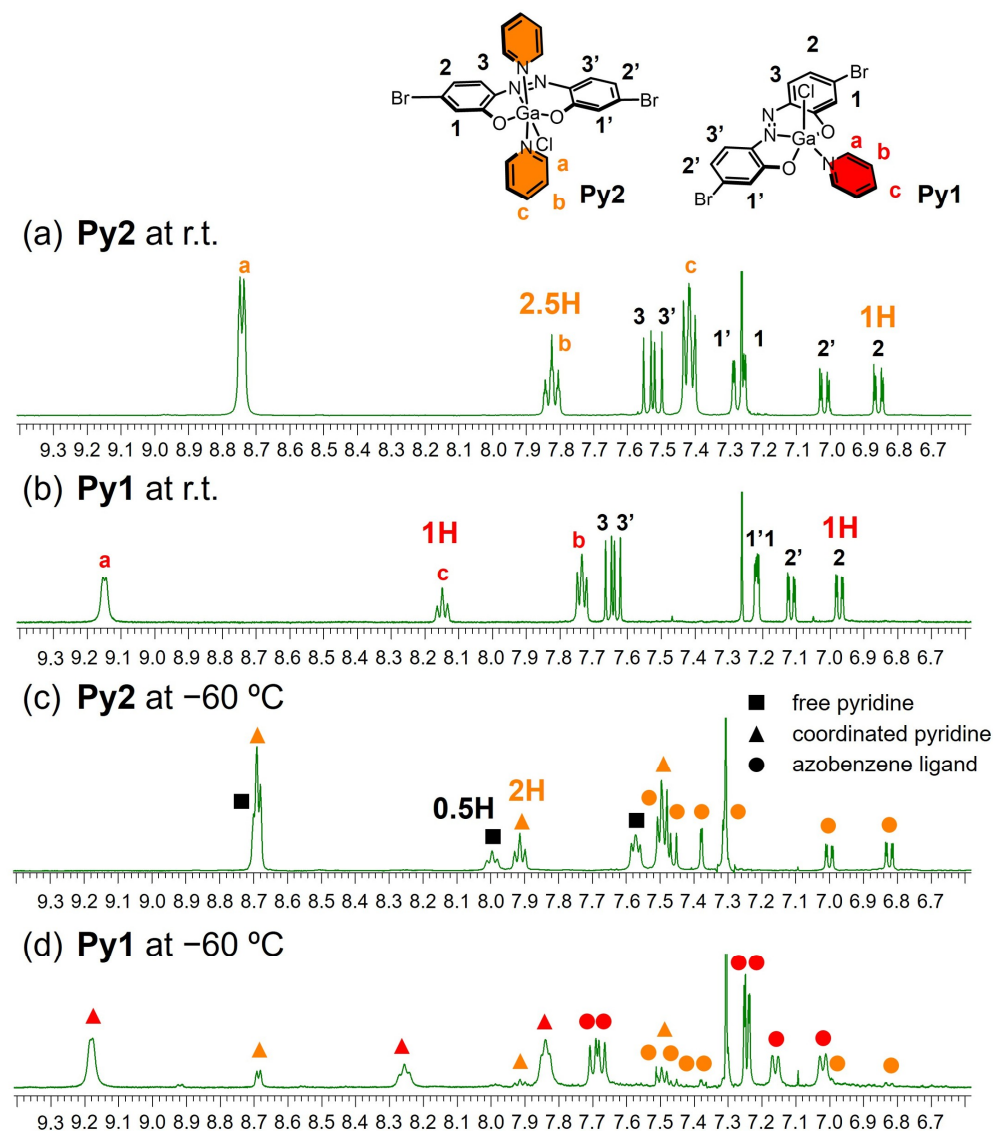


Figure 3. ^1H NMR spectra of gallium complexes, (a, c) **Py2** and (b, d) **Py1** obtained at (a, b) room temperature and (c, d) $-60\text{ }^{\circ}\text{C}$ in CDCl_3 with the peak assignments (free pyridine: ■, coordinated pyridine: ▲, azobenzene ligand: ●). The orange, red, and black symbols denote the signals from **Py2**, **Py1**, and free pyridine, respectively.

Optical Properties

UV-vis absorption and fluorescence (FL) spectra and absolute fluorescent quantum yields (Φ_{FLS}) of the three complexes **Py0**, **Py1** and **Py2** were measured in dichloromethane (DCM) ($1.0 \times 10^{-5}\text{ M}$). **Py0** and **Py1** were prepared in the glove box because they were moisture sensitive in solution. It was revealed that the optical properties of **Py0** and **Py1** were different, meanwhile those of **Py1** and **Py2** were almost the same (Figure 4a, 4b). To evaluate the coordination behavior in solution, the

titration experiment was performed with **Py0** as the starting compound with pyridine (Figure 4c, 4d). The results showed a two-step change with the isosbestic points at 359 nm and 461 nm (0.5–10 eq.) in the first step and at 331 nm and 530 nm in the second step (10–5000 eq.). The reason why isosbestic point did not appear between 0–0.5 eq. might be due to dimerization of **Py0**¹⁵, and a gradual change in absorption was observed as time elapsed from the moment of dissolution absorption (Figure S6). Based on these results, it is considered that the first step indicates the formation of **Py0** to **Py1**, and the second step involves the formation of **Py1** to **Py2**. From the UV–vis absorption titration spectra (Figures 4c and S7), the binding constants were estimated to be $1.9 \times 10^6 \text{ M}^{-1}$ for the first step and 93 M^{-1} for the second step (Figures S8 and S9). Furthermore, an increase in luminescence intensity was monitored as the amount of pyridine increased (Figure 4d). Additionally, at 1000 eq. or less, the volume of pyridine in the solution is less than 1%, therefore the solvent effect can be considered negligible. Within this range, the two-step change was saturated, and significant change was hardly observed between 1000 eq. and 5000 eq., indicating that this change should be due to coordination rather than solvent effects. Considering the fact that optical properties of **Py1** and **Py2** were identical, **Py2** should dissociate in solution to form **Py0** and **Py1** under dilute conditions (Figure 4a, 4b). In other words, **Py0**, **Py1**, and **Py2** coexist as an equilibrium state in the solution state. It was also found that an excess amount of pyridine was required to form a fully six-coordinated state at the optically measured concentration. Next, we examined the optical properties under the conditions of mainly four-coordinated state (**Py0** in DCM), five-coordinated state (**Py1** in DCM), and six-coordinated state (**Py2** in pyridine) (Figure 5 and Table 1). It was shown that the values of Stokes shift decreased and the quantum yield increased, by increasing the coordination number from four to five and six as observed in the titration.

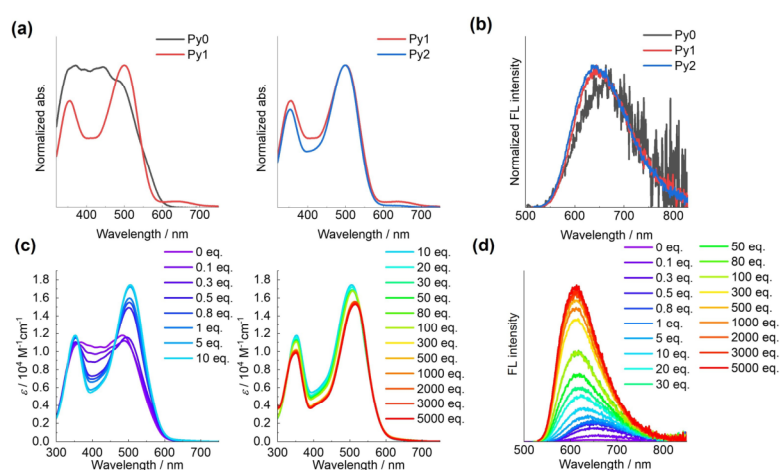


Figure 4. (a) Comparisons of normalized UV–vis absorption and (b) FL spectra of **Py0**, **Py1**, and **Py2** in DCM (1.0×10^{-5} M). (c) UV–vis absorption and (d) FL titration spectra of pyridine with **Py0** in DCM (1.0×10^{-4} M).

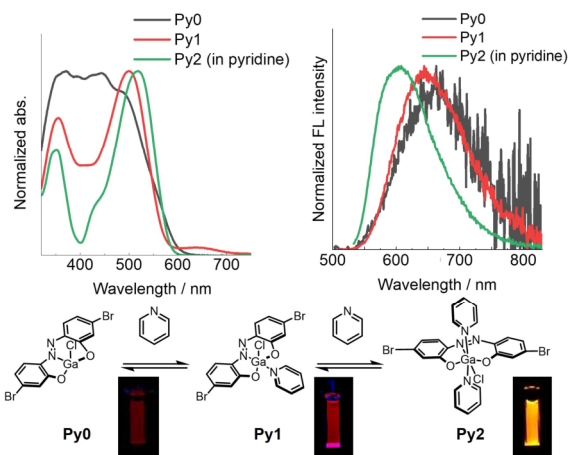


Figure 5. Normalized UV-vis absorption and FL spectra of **Py0**, **Py1** in DCM and **Py2** in pyridine/DCM = 99/1 v/v (1.0×10^{-5} M).

Table 1. Optical data of **Py0**, **Py1**, and **Py2**

	$\lambda_{\text{abs}}^{\text{a}}$ / nm	$\lambda_{\text{FL}}^{\text{a}}$ / nm	Stokes shift $^{\text{b}}$ / cm^{-1}	$\Phi_{\text{FL}}^{\text{c}}$ / %
Py0	488	663	5408	<0.1
Py1	498	644	4552	2.5
Py2	518	608	2858	22.6

^a In DCM (1.0×10^{-5} M), excited at λ_{abs} for FL.

^b $1 / \lambda_{\text{abs}} \times 10^7 - 1 / \lambda_{\text{FL}} \times 10^7$.

^c Absolute FL quantum yield, excited at 488 nm for **Py0**, at 498 nm for **Py1**, and at 518 nm for **Py2**.

DFT Calculation

We performed quantum chemical calculation with density functional theory (DFT) to theoretically investigate the causes of the decrease in the Stokes shift and the increase in the quantum yield (Figure 6a). In both **Py1** and **Py2**, the HOMO–LUMO transitions correspond to the π – π^* transition,³⁶ and luminescence should be observed from the azobenzene-based π -conjugated framework. The results of the calculation also supported that shorter emission wavelengths of **Py2** than those of **Py1** are attributed to the formation of a higher coordinated state. Furthermore, according to the optimized structures of **Py1** and **Py2** in the S_0 and S_1 states, it is assumed that the smaller structural relaxation should occur in **Py2** than **Py1** because structural differences are smaller in **Py2** (Figure 6b). As a representative value, the O–Ga–O bond angle from S_0 to S_1 increases by 13° for **Py1**, while that by 4° for **Py2**. These results indicate that the suppression of structural relaxation of the azobenzene moiety should be responsible for the decrease in the Stokes shift and the increase in the quantum yield of **Py2**. Although the same

calculation was also attempted for **Py0**, the optimized structure in the S_1 state did not converge. This implies that the structural relaxation might be extremely large, leading to the quench of emission from **Py0**.

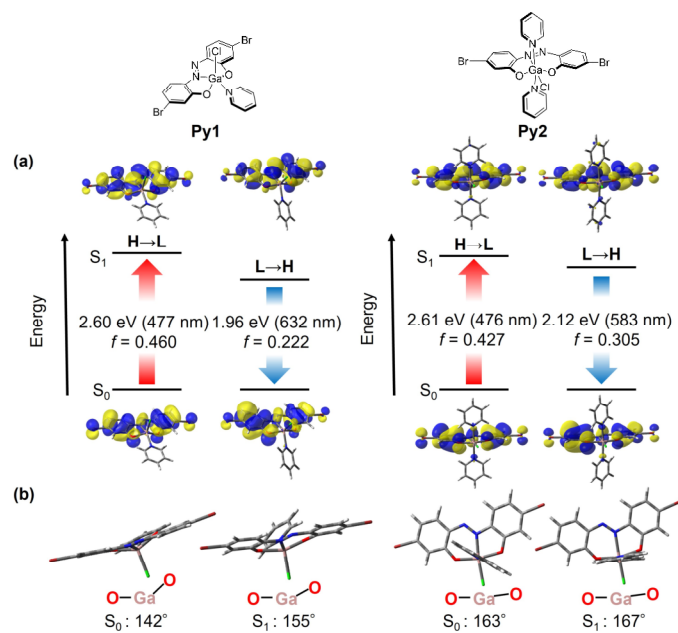


Figure 6. (a) Transition energies and oscillator strengths (f) of $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_0$ transitions from the optimized structures in the S_0 and S_1 states of **Py1** and **Py2**, respectively, with the most contributed MOs (H: HOMO, L: LUMO). (b) Variation of O–Ga–O bond angle between optimized structures in the ground (left) and excited states (right).

Bidentate Ligands

It was found that the coordination number can be changed to four, five, and six by the coordination of pyridine, and structural relaxation followed by the enhancement of luminescence property can be induced as increasing the valence bonds. Based on these observations, we hypothesized that the introduction of a bidentate ligand might contribute to strong restriction to structural relaxation by its chelating effect, followed by intense emission properties. To evaluate validity of this presumption, we synthesized the gallium complexes, **Phen** and **Bipy**, using 1,10-phenanthroline and 2,2'-bipyridyl as bidentate ligands, respectively. **Phen** and **Bipy** were prepared through ligand exchange from **Py2** in MeCN and DCM solvents in the presence of each ligand, respectively. From the SC-XRD measurements, it was confirmed that both **Phen** and **Bipy** formed the six-coordinated octahedral geometries with Cl atom perpendicular to the π -plane because of the construction of the five-membered rings involving the bidentate ligands (Figure 7). The bond lengths of Ga–X (X = N, O, and Cl) are longer than the covalent bond and shorter than the sum of van der Waals radii, indicating the formation of the hypervalent state of gallium, similarly to **Py2**. The detailed crystallographic data are shown in Tables S4 and S5, Figures S4 and S5.

Optical measurements were performed with **Phen** and **Bipy** in DCM (Figure 8). Accordingly, compared to **Py2**, the smaller Stokes shifts were observed from both **Phen** and **Bipy**, and the largest quantum yield was observed from **Phen** of the three complexes (Table 2). This indicates that the strong coordination of the bidentate ligand through the chelating effect can crucially suppress structural relaxation. This phenomenon was also supported by the DFT calculation as in the previous section (Figure S14). In **Bipy**, the quantum yield was almost the same as that of **Py2**, implying that molecular motions might occur due to low planarity of the 2,2'-bipyridyl ligand.

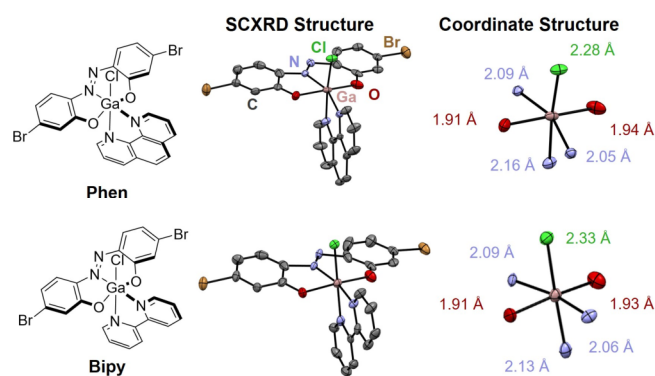


Figure 7. ORTEP drawings of **Phen** and **Bipy** (50% probability for thermal ellipsoids). Hydrogens and disordered atoms are omitted for clarity. The bond lengths of Ga–X (X = N, O, and Cl) are described. All crystallographic data are shown in the Supporting Information.

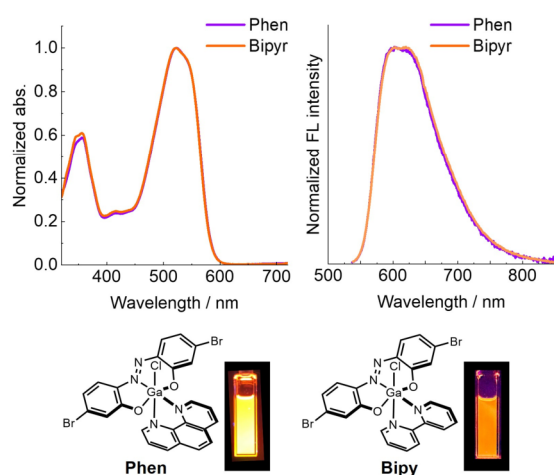


Figure 8. Comparisons of normalized UV–vis absorption and FL spectra of **Phen** and **Bipy** in DCM (1.0×10^{-5} M).

Table 2. Optical data of **Phen** and **Bipy**

	$\lambda_{\text{abs}}^{\text{a}}$ /nm	$\lambda_{\text{FL}}^{\text{a}}$ /nm	Stokes shift $^{\text{b}}$ / cm^{-1}	$\Phi_{\text{FL}}^{\text{c}}$ /%
Phen	523	602	2509	37.7
Bipy	522	603	2573	22.7

^a In DCM (1.0×10^{-5} M), excited at λ_{abs} for FL.

^b $1 / \lambda_{\text{abs}} \times 10^7 - 1 / \lambda_{\text{FL}} \times 10^7$.

^c Absolute FL quantum yield, excited at 523 nm for **Phen**, at 522 nm for **Bipy**.

The effect of coordinating solvent

As described in the above sections, the electronic structures followed by optical properties of the conjugated systems involving hypervalent gallium can be perturbed by the ligands. To gain deeper insight into the effect of ligand coordination on electronic properties, we performed optical measurements in various solvents. Then, we focused on the influence of the donor number (DN) which is defined as the negative enthalpy value with kcal mol^{-1} as a unit in the addition reaction between a solvent molecule as a Lewis base and the standard Lewis acid SbCl_5 as a measure of Lewis basicity.^{37,38} To compare the effect of Lewis basicity, we paid attention to the results in solvents with different DN, pyridine ($\text{DN} = 33.1 \text{ kcal mol}^{-1}$), DMSO ($\text{DN} = 29.8 \text{ kcal mol}^{-1}$), tetrahydrofuran (THF) ($\text{DN} = 20.0 \text{ kcal mol}^{-1}$), and methanol (MeOH) ($\text{DN} = 19.0 \text{ kcal mol}^{-1}$). In **Py0** and **Py1**, we found that they were partially decomposed when using a relatively low DN such as MeOH, and therefore optical properties such as UV-vis absorption and FL spectra and Φ_{FL} s were monitored after ligand exchange from pyridine to each solvent molecule using **Py2** as an initial state. It was found that the quantum yields increased as increasing solvent DN (Figure 9 and Table 3). Importantly, in non-coordinating solvent, significant spectral differences were hardly observed between non-polar solvent, toluene and polar solvent, DCM, meaning that the solvent polarity has little effect on the optical properties. In addition, the result that the quantum yield was slightly higher in THF than in MeOH suggests that DN strongly influences quantum yields, regardless of whether the solvent is protonic or non-protonic even when considering the effects of hydrogen bonding across various solvents. In summary, it is clearly indicated that although the electronic properties of the hypervalent gallium complexes can be greatly changed by coordination, similarly to other hypervalent azobenzene complexes, in the case of gallium, it should be emphasized that larger perturbation can be induced by coordination with the solvent having the stronger Lewis basicity.

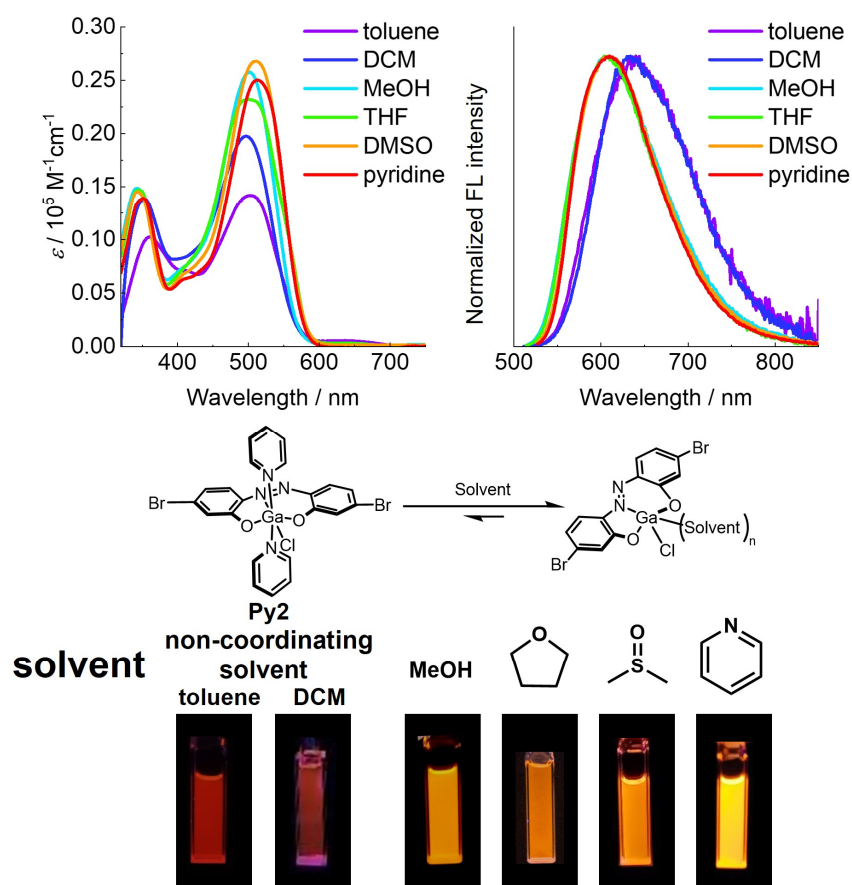


Figure 9. Comparisons of normalized UV-vis absorption and FL spectra of **Py2** in toluene/solvent = 1/99 v/v (1.0×10^{-5} M).

Table 3. Optical data of **Py2** in various solvents

Solvent	DN /kcal mol ⁻¹	$\lambda_{\text{abs}}^{\text{a}}$ /nm	$\lambda_{\text{FL}}^{\text{a}}$ /nm	Stokes shift ^b / cm ⁻¹	$\Phi_{\text{FL}}^{\text{c}}$ /%
toluene	0.1	498	640	4455	2.5
DCM	1.0	496	636	4438	3.2
MeOH	19.0	501	609	3540	4.5
THF	20.0	496	604	3604	4.9
DMSO	29.8	511	608	3122	19.0
pyridine	33.1	512	607	3057	26.4

^a Toluene/solvent = 1/99 v/v (1.0×10^{-5} M), excited at λ_{abs} for FL.

^b $1 / \lambda_{\text{abs}} \times 10^7 - 1 / \lambda_{\text{FL}} \times 10^7$.

^c Absolute FL quantum yield, excited at 498 nm for toluene, at 496 nm for DCM, at 501 nm for MeOH, at 494 nm for THF, at 511 nm for DMSO, at 512 nm for pyridine.

Application

Finally, based on the ability to enhance luminescence depending on the coordination, we constructed a facile testing system for Lewis basicity of solvents. A filter paper was soaked on the dilute solution of **Py0** (1.0×10^{-4} M), and after drying,

a sensing paper was obtained. For testing, target solvents were dropped on a sensing paper, and by evaluating emission intensity at the dropping positions under UV irradiation (365 nm), we estimated DN. Accordingly, intense orange luminescence was observed from the points where large DN solvents were dropped, while weak luminescence was detected with relatively smaller DN solvents (Figure 10 and Movie 1). On the other hand, for solvents with low coordination properties, we observed ring-shaped luminescence due to low solubility and diffusion. Faint luminescence was observed with non-coordinating solvents. Notably, emission behaviors were able to be preserved under ambient conditions for several seconds. The filter paper remained usable for at least one week after preparation under the atmosphere and indoor lighting. If the coordinated solvent can be removed by vacuum extraction, reuse of the paper should be possible. These results indicate that the facile and the rapid evaluating system for Lewis basicity of solvents can be established based on the coordination-triggered luminescent changes of the hypervalent gallium complex.

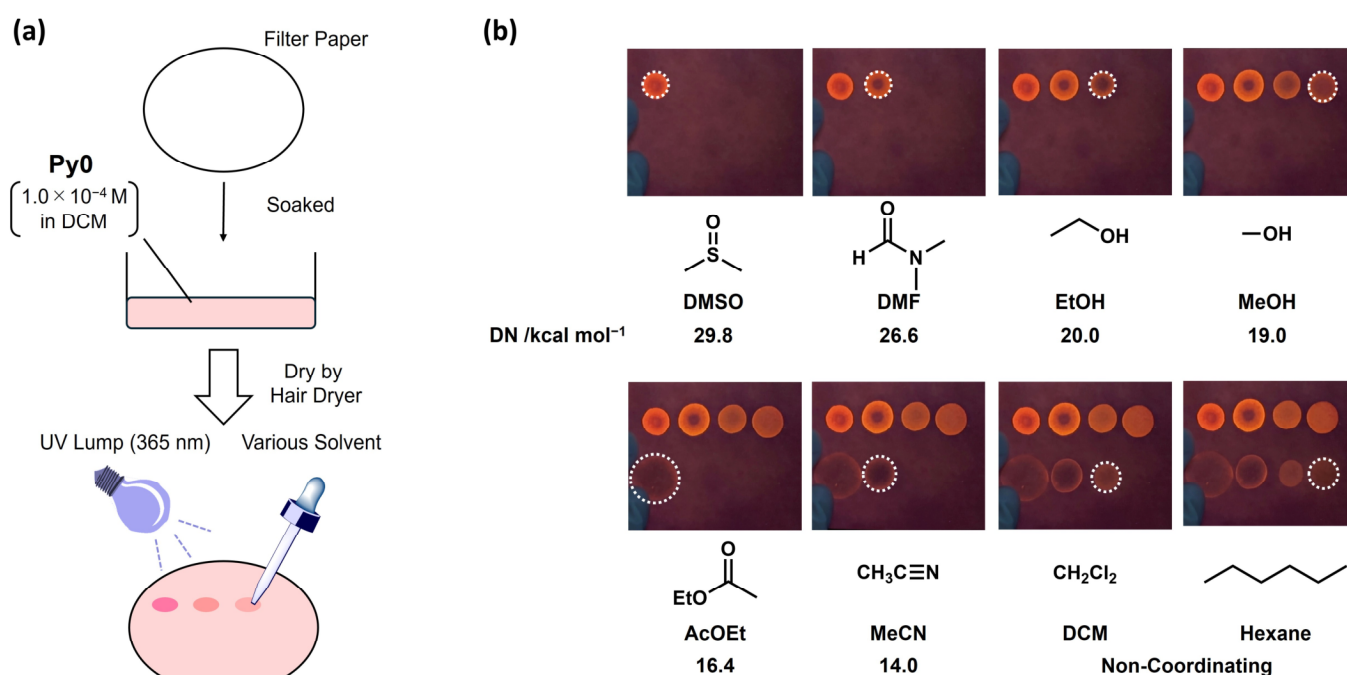


Figure 10. (a) Preparation method for the **Py0** soaked filter paper and (b) application to check the strength of Lewis basicity of each solvent.

Conclusion

We synthesized hypervalent gallium complexes with azobenzene. **Py2** exhibited stepwise pyridine elimination by heating, leading to the production of **Py1** and **Py2** from **Py2** by controlling pyridine coordination. From optical measurements, it was shown that as the number of coordinated pyridine increased, narrower Stokes shifts and smaller emission quantum yields were observed. From quantum chemical calculations, it was revealed that the suppression of structural relaxation in the six-coordinated structure than in the five-coordinated structure should play a key role in optical changes by the coordination. In addition, the complex with a rigid bidentate ligand, **Phen**, showed the largest emission efficiency (37.7%) owing to the strong coordination with the chelating effect followed by suppression of molecular motions in the excited state. Furthermore, since the tuning of luminescence quantum yields by ligand exchange was achieved with multiple solvents, we demonstrated the use of it as a luminescent turn-on sensor to easily compare the strength of the Lewis basicity of the solvents. These results confirm the interesting phenomenon that the use of gallium, having Lewis acidity, transfers the coordinated state on the element to the degree of structural relaxation of the π -conjugated systems. Our findings suggest that the use of heavy main-group elements can further extend the functionality of the π -conjugated system.

Supporting information

Experimental details “GaAzCl_SI.pdf”.

Acknowledgment

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Accession Codes

CCDC (**Py1**, **Py2**, **Phen**, and **Bipy**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033

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The introduction of main-group elements into the π -conjugated systems enables the modulation of optical properties based on changes in the coordinated state of the elements, and the use of heavy elements with high Lewis acidity is expected to extend the range of coordination response. Herein, we synthesized hypervalent gallium azobenzene complexes and found that they can be used as turn-on luminescent sensors to visualize the strength of solvent Lewis basicity. The absolute fluorescence quantum yields were improved by suppressing structural relaxation, and the values rose not only as increasing the coordination number but also as enhancing the Lewis basicity.

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