

Effects of a Central Element on Photoluminescence Properties of β -Diketimate Complexes Composed of the Group 13 Elements

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Abstract

Various kinds of boron complexes have been utilized as functional luminescent materials. However, only a limited number of emissive complexes containing the other group 13 elements have been reported. Herein, we report synthesis and optical properties of luminescent β -diketiminato complexes containing a series of the group 13 elements. The synthesized complexes exhibited crystallization-induced emission properties. It was indicated that the heavier group 13 elements accelerate intersystem crossing from singlet to triplet excited state because of the strong heavy atom effect. Finally, we discovered that aluminum and gallium complexes can work as a solid-state luminescent material with high emission efficiencies.

Introduction

The introduction of p-block elements to π -conjugated systems is one of the attractive research topics in the fields of fundamental organoelement chemistry and material chemistry.¹⁻⁸ Particularly, as boron possesses a vacant p orbital, which can afford to interact with π -conjugated systems and with Lewis bases, various optical and electronic functions have been achieved based on boron-containing π -conjugated compounds, such as efficient luminescence,⁹ aggregation-induced emission (AIE),¹⁰ phosphorescence,¹¹ thermally activated delayed fluorescence,¹² near-infrared emission,¹³ and n-type semiconductivity.¹⁴ Meanwhile, the other group 13 elements have also been utilized for obtaining optoelectronic materials. For instance, aluminum tris(8-quinolinolate), Alq₃, has been extensively studied as light-emitting and electron-transporting layers in organic light-emitting diodes.¹⁵ Moreover, it was reported that the heavier congeners, gallium and indium complexes, were able to be applied for electroluminescent materials. The device with gallium tris(8-quinolinolate) (GaQ₃) exhibited an approximately 50% higher power efficiency than that with Alq₃. This is possibly because GaQ₃ possesses the higher charge-transporting property originating from the higher injection efficiency of charge carriers into GaQ₃.¹⁶ In addition, it was also demonstrated that some dipyrroin-based indium complexes exhibited more efficient photoluminescence than the lighter congeners¹⁷ and stimuli-responsive emission which is absent in the gallium one.¹⁸ These results strongly encourage us to develop functional materials based on the heavier group 13 element

complexes. On the other hand, although five- and six-coordinated complexes of the heavier group 13 elements have been systematically studied in some cases, the examples of four- or less coordinated species are still limited, probably because heavy element complexes often form structurally undefined species¹⁸ or decompose during optical measurements.¹⁹

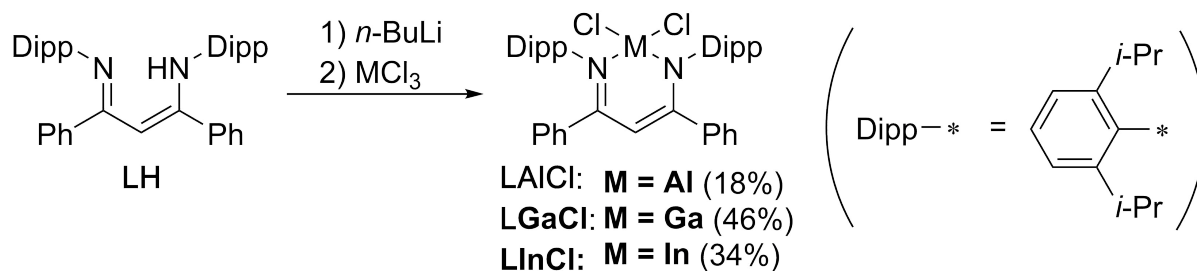
Recently, we have synthesized boron,²⁰ aluminum, gallium and indium²¹ complexes of β -dialdiminate ligand and revealed that the type of group 13 elements affects the absorption and emission wavelengths and the stimuli responsiveness toward Lewis bases.²¹ Although dynamic ligand exchange reactions were also observed in the indium complex, it was implied that the natural charge at a central element could be a practical measure for assessing the effects of elements on the photophysical properties. Furthermore, we have reported that the four-coordinated β -diketiminato (DKI) complexes of the group 13 elements exhibit fruitful optical properties, such as AIE and crystallization-induced emission (CIE),^{22–26} vapochromic luminescence,^{27,28} and mechanochromic luminescence.²⁹ Interestingly, boron complexes showed slight luminochromism, whereas the gallium complex presented sensitive luminochromic behavior toward volatile organic compounds.²⁷ To understand these differences in optical properties between the central elements, fundamental studies are needed regarding the element type–property relationship with the same group elements. Importantly, DKI ligands have enabled to access variety of four-coordinated complexes of the heavier group 13 elements because their electronic and steric demands can be easily tuned by the substituents.³⁰ Therefore,

we presumed that DKI ligands are an optimum scaffold for systematically studying the effects of central elements on the photophysical properties of complexes. Here we provide a systematic comparison on the optical properties of (DKI)MCl₂ (M = Al, Ga, In), where the π -conjugated DKI ligand was decorated with the sterically hindered 2,6-diisopropylphenyl (Dipp) group at the imine nitrogen atoms. We synthesized complexes and found that the aluminum and gallium complexes showed clear emission enhancements by crystallization. In contrast, the indium complex exhibited slight emission in both solution and crystal at room temperature. It was proposed that the strong spin–orbit coupling derived from the heavy indium atom significantly affects the photophysical process of the complex. We also observed that aluminum and gallium complexes have intense solid-state luminescent ability.

Results and Discussion

In order to obtain stable and CIE-active complexes, the sterically hindered, π -conjugated ligand **LH** bearing the Dipp group at the imine N atoms was employed. The synthesis of **LH** was carried out using the reported procedure.³¹ Dichloroaluminum, dichlorogallium and dichloroindium DKI complexes were prepared by the reaction of *n*-butyllithium and the ligand followed by the treatment with the corresponding metal trichlorides (Scheme 1). All products were readily soluble in toluene, benzene and chloroform, and sparingly soluble in hexane. NMR spectroscopy revealed that their four-coordinated structures were maintained even in solution at room temperature. These complexes were stable both in solution and solid states under inert atmosphere but are air- and moisture-sensitive.

Scheme 1. Synthetic schemes of the dichlorometal DKI complexes



To glean detailed information with respect to the coordination environment, the molecular structures of the complexes were determined using single-crystal X-ray analysis. Suitable single crystals for analysis were grown from hexane solutions by a slow evaporation method in a

glovebox. ORTEP of the complexes and their packing structures are shown in Figure 1, and data collection parameters and refinement statistics are listed in Table S1. It should be noted that the qualities of the refinement for the aluminum and gallium complexes were relatively low probably due to their low stability toward X-ray irradiation. Therefore, the following discussion is partly qualitative. All the complexes were crystallized in the monoclinic space group $P2_1/n$ and each asymmetric unit included one crystallographically independent molecule.

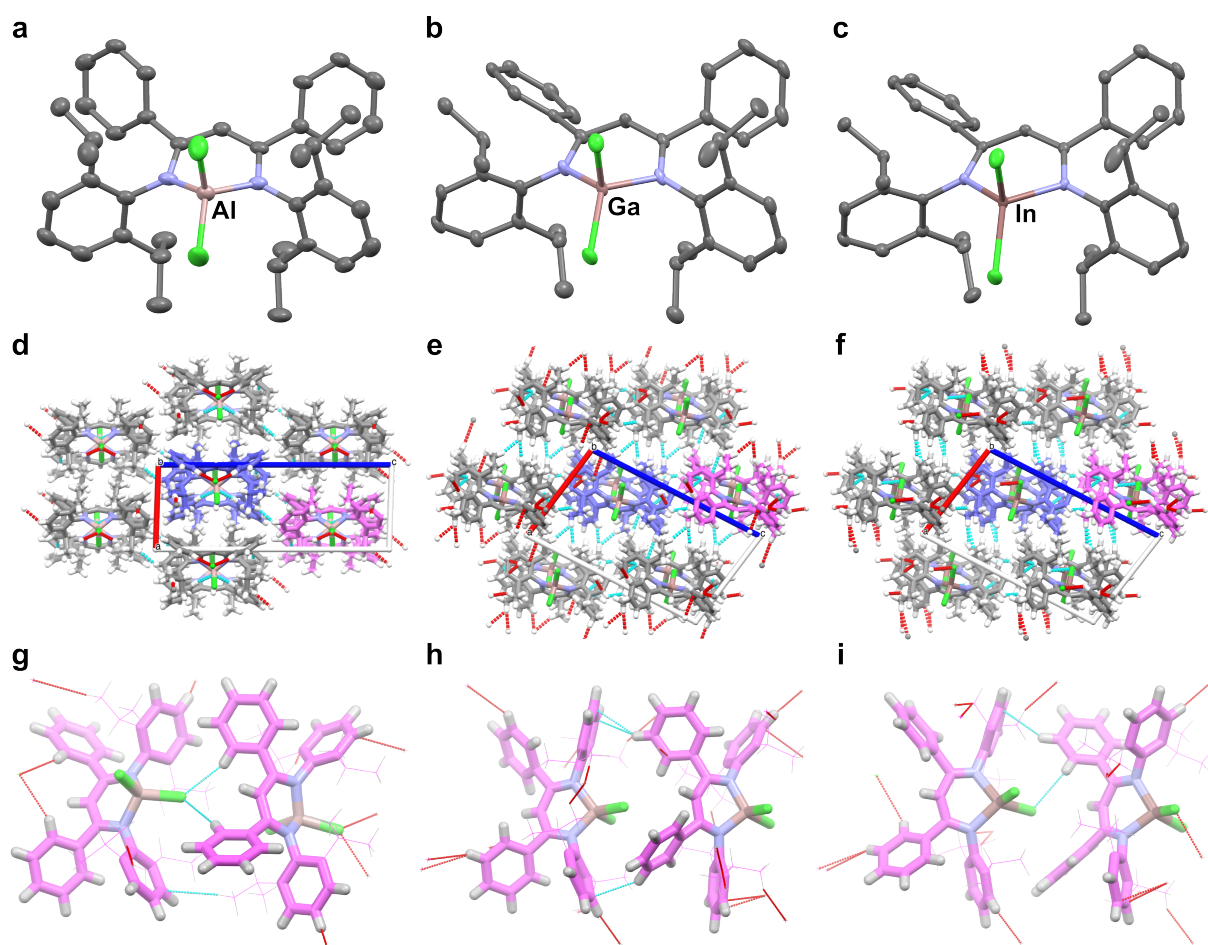
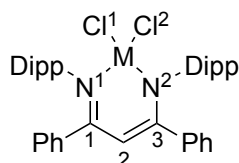


Figure 1. ORTEP of (a) **LAICl**, (b) **LGaCl** and (c) **LInCl** (ellipsoids drawn at 50% probability level). All hydrogen atoms were omitted for clarity. Packing structures of (d) **LAICl**, (e) **LGaCl** and (f) **LInCl** along the *b* axis. Cyan and red dotted lines represent short contacts within shown molecules and with outside molecules, respectively. Intermolecular interactions between nearest-neighbor molecules of (g) **LAICl**, (h) **LGaCl** and (i) **LInCl**. Isopropyl groups are shown in wireframe for clarity.

Selected bond distances and angles are listed in Table 1. These complexes show the typical structural features of the class of group 13 metal DKI complexes:³² (i) The C₃N₂ ring moiety is nearly planar. (ii) The metal ions are displaced from the C₃N₂ plane. (iii) The bond lengths of C–C and C–N in the ring are within the narrow ranges 1.396(7)–1.410(2) and 1.338(2)–1.355(6) Å, indicating considerable multiple character in these bonds. (iv) Focusing on the C₃N₂M ring, we found that the N–M–N angle is invariably the narrowest ($\leq 100^\circ$), whereas the other angles are all *ca.* 115° and more with the widest angle (*ca.* 130°) observed at the C2 carbon.

Table 1. Selected bond distances (Å) and angles (°) for the complexes



Bond	LaCl	LGaCl	LIInCl
M–Cl1	2.126(2)	2.148(1)	2.3233(5)
M–Cl2	2.106(2)	2.179(1)	2.3527(5)
M–N1	1.869(4)	1.932(4)	2.122(1)
M–N2	1.867(4)	1.929(4)	2.119(1)
N1–C1	1.352(6)	1.343(6)	1.338(2)
N2–C3	1.355(6)	1.340(6)	1.338(2)
C1–C2	1.405(7)	1.408(6)	1.410(2)
C2–C3	1.396(7)	1.403(6)	1.408(2)
Angle	LaCl	LGaCl	LIInCl
N1–M–N2	100.4(2)	100.5(2)	94.58(5)
Cl2–M–Cl1	112.06(9)	111.00(5)	112.76(2)
N1–M–Cl1	108.7(1)	106.1(1)	106.07(4)
N2–M–Cl1	108.7(1)	110.5(1)	113.15(4)
N1–M–Cl2	113.3(1)	114.9(1)	114.90(4)
N2–M–Cl2	113.0(1)	113.2(1)	113.89(4)
M–N1–C1	114.7(3)	115.1(3)	116.3(1)
M–N2–C3	114.3(3)	116.0(3)	116.4(1)
N1–C1–C2	122.0(4)	122.9(4)	124.0(1)
N2–C3–C2	122.3(4)	124.0(4)	125.8(1)
C1–C2–C3	129.6(4)	129.6(4)	131.8(1)

The crystal structures of all complexes are comparable with each other and composed of a bundle-like structure along the *b* axis, which is parallel to the C_2 axis (Figure 1d–f and Figure S1). Some CH– π and CH–halogen interactions were found to form each strand in the bundle (Figure 1g–i). In addition, only CH–H and CH–C contacts were observed between the strands. It should be noted that less significant π – π interaction were observed in the crystal structures of all complexes. Hence, it can be assumed that there is no notable overlapping of π orbitals of the conjugation systems between the molecules. Therefore, intermolecular electronic interactions should not remarkably affect the photophysical properties.

To investigate the photophysical properties of the synthesized complexes, UV–vis absorption and photoluminescence spectra of the dilute solutions (2-methylpentane/toluene, 99/1, 1×10^{-5} M) were recorded (Figure 2). A slight bathochromic shift of the wavelengths at the absorption maxima was observed as the metals became heavier, whereas the molar absorption coefficients were hardly changed by altering the type of the central metals. This observation suggests that the electronic nature of the S_0 – S_1 transition is hardly affected by the alteration of the central metal, because the transition should be originated mainly from the transition between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the ligand moiety (Figure 2d).²⁵ Importantly, all the complexes hardly showed photoluminescence at room temperature in the dilute solutions. The absolute photoluminescence quantum yields were below the detection limit (< 0.01). In contrast, the frozen glassy solutions (77 K) of the

complexes showed nearly quantitative luminescence (Table 2). In the photoluminescence spectra of the complexes at 77 K, two distinct luminescence bands were observed at 428–459 and 516–531 nm. The results from the luminescence lifetime measurements revealed that the peaks in the shorter wavelength region were assigned to fluorescence with nanoseconds-order lifetimes, and the others in the longer wavelength region were attributed to phosphorescence because of the significantly longer lifetime (Table 3).

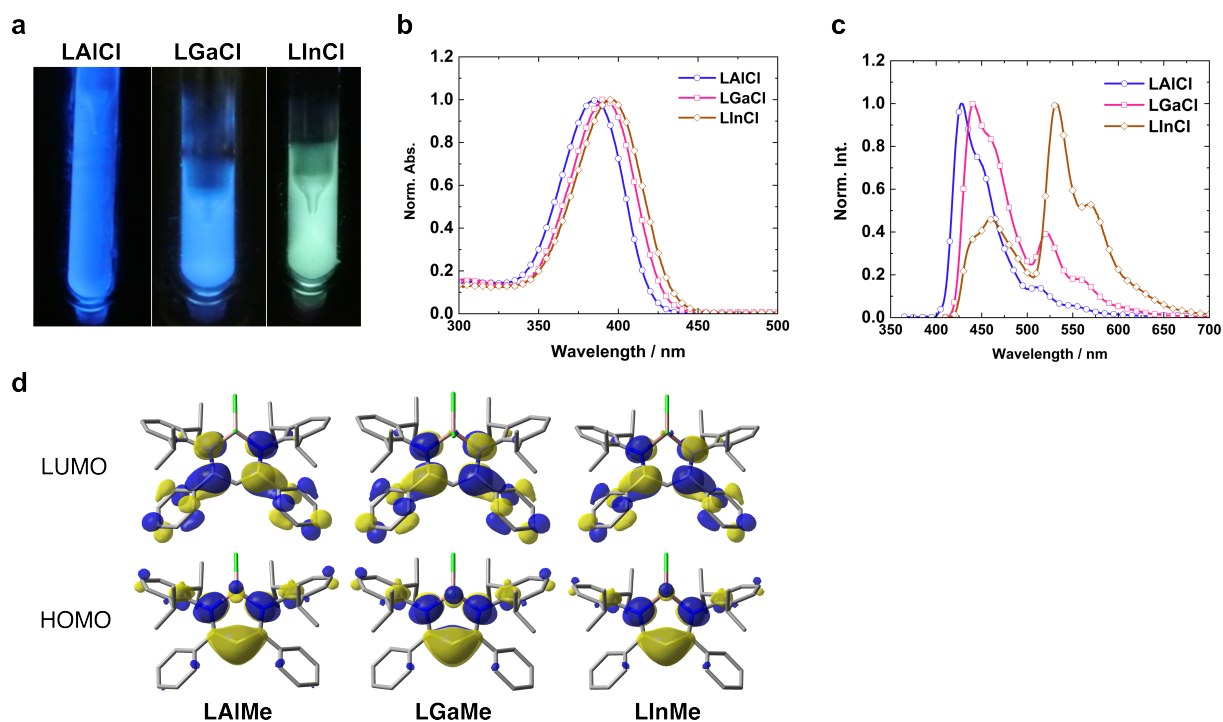


Figure 2. (a) Pictures of the solutions of the complexes at 77 K under UV irradiation. (b) Normalized UV-vis absorption spectra at room temperature and (c) normalized photoluminescence spectra at 77 K of **LAI**, **LGA** and **LIN** in the dilute solutions (2MP/toluene = 99/1, 1×10^{-5} M). (d) Kohn-Sham HOMO and LUMO distributions of the complexes. Calculation: PBE1PBE/Lanl2DZ for In and def2-TZVP for the other elements//CAM-B3LYP/Lanl2DZ for In and 6-31+G(d,p) for the other elements.

Table 2. Photophysical properties of the complexes in the dilute solutions

	room temperature		77 K	
	$\lambda_{\text{abs}} / \text{nm}$	$\varepsilon / 10^4 \text{ M}^{-1} \text{ cm}^{-1}$	$\lambda_{\text{Fluo}}; \lambda_{\text{Phos}} / \text{nm}$	$\Phi_{\text{Fluo}}; \Phi_{\text{Phos}}$
LAICl	386	3	428; 516	0.90; 0.10
LGaCl	390	3	441; 522	0.73; 0.27
LInCl	395	3	459; 531	0.34; 0.66

Table 3. Fluorescence and phosphorescence lifetimes of the complexes in solutions at 77 K

	Fluorescence ^a				Phosphorescence ^b			
	τ_1 / ns f_1^c	τ_2 / ns f_2^c	τ_3 / ns f_3^c	$\langle \tau \rangle / \text{ns}^d$	τ_1 / ms f_1^c	τ_2 / ms f_2^c	τ_3 / ms f_3^c	$\langle \tau \rangle / \text{ms}^d$
LAICl	1.32 9.58%	3.32 83.27%	— ^e	2.9	207 77.9%	725 22.1%	— ^e	320
LGaCl	1.84 3.51%	3.69 96.49%	— ^e	3.6	79 100%	— ^e	— ^e	79
LInCl	0.11 3.23%	1.49 38.94%	3.28 57.82%	2.5	5.3 1.20%	19 62.9%	36 35.9%	25

^aExcited at 375 nm with an LED laser and detected at λ_{Fluo} . Decay curves were fitted with the

multi-component exponential function: $I(t) = \sum_i [\alpha_i \exp(-\tau_i/t)]$. ^bPhosphorescence lifetimes were

estimated by using time-resolved photoluminescence decay measurements detected at λ_{Phos} .

^cFraction of component i : $f_i = \alpha_i \tau_i / \sum_i \alpha_i \tau_i$. ^dAverage lifetime: $\langle \tau \rangle = [\sum_i \alpha_i \tau_i^2] / [\sum_i \alpha_i \tau_i] = \sum_i f_i \tau_i$.

^eNot used.

LAICl and **LGaCl** showed the clear CIE effect, while the crystal of **LInCl** exhibited slight emission at room temperature (Figure 3). The absolute photoluminescence quantum yields of the crystals were determined to be 0.48 for **LAICl**, 0.57 for **LGaCl**, and below the detection limit (< 0.01) for **LInCl**. The emission bands from these crystals were all assigned to fluorescence because of their short lifetimes. These observations clearly indicate that the intra- and intermolecular vibrational quenching of the excited states should be restricted at room temperature by the crystallization except for the case of **LInCl**. In contrast to the situation at room temperature, the crystals of all complexes emitted intensely at 77 K (Figure 3 and Table 4). Dual emission properties of fluorescence and phosphorescence were observed from all the complexes as well as the solutions.

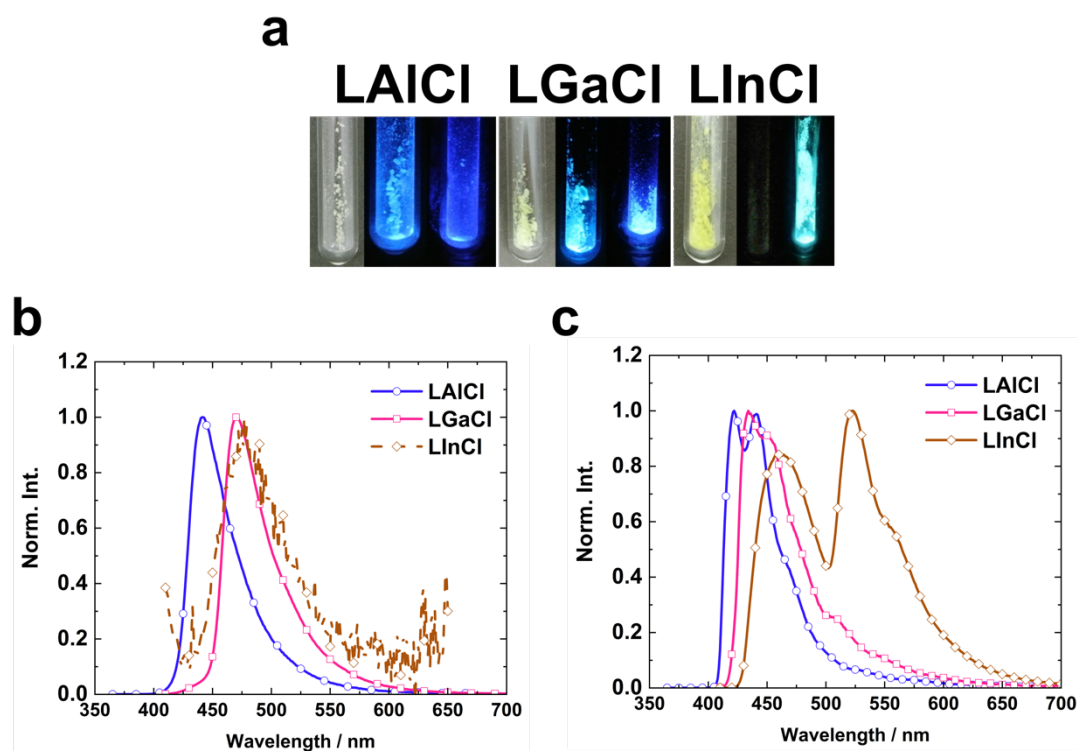


Figure 3. (a) Pictures of the crystals of **LAICI**, **LGaCl** and **LInCl** under natural light (left panels) and UV irradiation at room temperature (middle panels) and 77 K (right panels). Normalized photoluminescence spectra of the crystals of the complexes at (b) room temperature and (c) 77 K.

Table 4. Photophysical properties of the complexes at crystalline states

	r.t.		77 K	
	$\lambda_{\text{Fluo}}; \lambda_{\text{Phos}} / \text{nm}$	$\Phi_{\text{Fluo}}; \Phi_{\text{Phos}}$	$\lambda_{\text{Fluo}}; \lambda_{\text{Phos}} / \text{nm}$	$\Phi_{\text{Fluo}}; \Phi_{\text{Phos}}$
LAICI	442; –	0.48; –	422, 441; 535	0.94; 0.06
LGaCl	470; –	0.57; –	434; 523	0.63; 0.19
LInCl	477; –	< 0.01; –	461; 523	0.37; 0.51

To gain further information about the differences in their optical properties, density functional theory (DFT) and time-dependent (TD-) DFT calculations were performed with the Gaussian 16 Rev. C³³ package. Geometry optimizations were performed with the CAM-B3LYP functional and the Lanl2DZ basis and its pseudopotential for In and the 6-31+G(d,p) basis set for the other elements. The electronic transition energies were calculated by TD-DFT with the PBE0 functional and the Ahlrichs def2-TZVP basis set³⁴ for all elements and the Lanl2DZ pseudopotential for In.³⁵ The experimental trend in S_0 – S_1 absorption maxima (**LAICl** < **LGaCl** < **LInCl**) were reproduced by the TD-DFT calculations (Table 5 and Figure 4a). The HOMO level was destabilized from –6.449 eV for **LAICl** to –6.405 eV for **LGaCl** and to –6.385 eV for **LInCl**, while the LUMO was changed from –2.161 eV to –2.131 and –2.121 eV, respectively (Figure 4b). As the S_1 state of all compounds was attributed to HOMO–LUMO transition, the red shift of their absorption band by increasing the atomic number could be ascribed to the destabilization of the HOMO rather than the change of the LUMO energy. Natural population analysis (NPA) revealed that the central element is less positively charged as the atomic number increases (Al > Ga > In, Table 5). Here, we used the NPA charges calculated with and without the pseudopotential to compare Ga and In and Al and Ga, respectively, because the comparison between the results from the different basis sets is not valid. Consequently, the destabilization of HOMO could be induced by the heavy atom and lead to the smaller energy of the HOMO–LUMO transition. It should be noted that the structure of the DKI moiety would not

significantly depend on the type of the central element. Therefore, the intrinsic nature of the central element would induce the differences in the photophysical properties.

Table 5. Results of (TD-)DFT calculations^a

	λ_{S0-S1} / nm	E_{S0-S1} / eV	f	E_{HOMO} / eV	E_{LUMO} / eV	NPA Charge on the metal atom
LaCl	330.1	3.7564	0.363	−6.449	−2.161	1.72
LGaCl	332.9	3.7248	0.395	−6.405	−2.131	1.57 (1.67) ^b
LiInCl	333.3	3.7194	0.440	−6.385	−2.121	1.64

^aPBE1PBE/def2-TZVP level of theory until otherwise noted. ^bThe value in the parentheses was obtained with the Lanl2DZ pseudopotential for Ga.

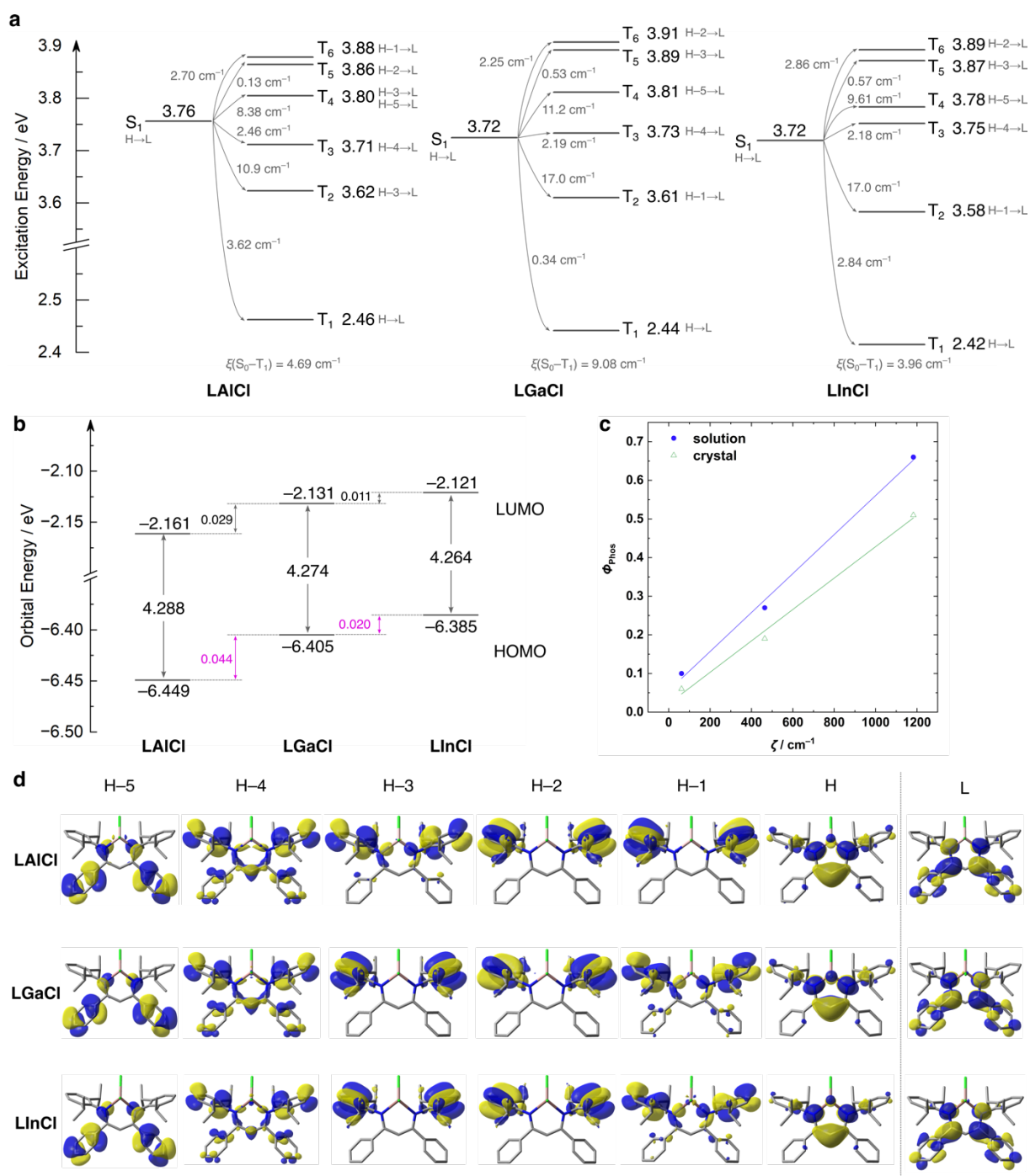


Figure 4. (a) Calculated singlet and triplet excited states. Main orbital contributions and spin-orbit coupling constants between S_m and T_n states ($\xi(S_m-T_n)$) are shown in gray texts. Excitation energies: Relative to the corresponding S_0 ground states. H and L denote HOMO and LUMO. (b) Calculated Kohn-Sham frontier orbital energies. (c) Plots of phosphorescence quantum yields of the solutions (blue filled circles) and the crystals (green open triangles) versus spin-orbit coupling constants.

orbit coupling constants ζ^{36} of the central group 13 metals. Lines are eye guides. (d) Selected Kohn–Sham molecular orbital distributions. Isovalue: 0.03.

It is worth noting that the phosphorescence quantum yields increase as the central elements become heavier for both the solutions and the crystals at 77 K (Tables 2 and 4). In addition, their phosphorescence lifetimes in solutions at 77 K are shortened as the atomic number increases (Table 3). These facts clearly indicate that the heavy atom effect plays an important role in their photophysical processes. Indeed, the phosphorescence quantum yields of the solutions and crystals clearly show the positive correlation against the SOC constant for a single atom (ζ , Figure 4c),³⁶ suggesting that the heavy atoms should lead to the acceleration of the intersystem crossing from singlet excited states to triplet ones. On the other hand, the large experimental values of the energy gap between S_1 and T_1 states (**LaCl**, 0.52 eV; **LGaCl**, 0.49 eV; **LiInCl**, 0.51 eV) seem to imply there might be other ISC processes through the higher triplet states. The series of TD-DFT calculations suggest that there are some accessible triplet states near the S_1 state, within *ca.* 0.1 eV, for all complexes (Figure 4a). To assess probability of ISC between S_1 and these triplet states, spin–orbit coupling (SOC) constants, ζ , were estimated with the Tamm–Dancoff approximation by using the Q-Chem 6.1 package.³⁷ The quite large ζ values for S_1 – T_2 and S_1 – T_4 transitions ($> 5 \text{ cm}^{-1}$) strongly support the fast ISC from the S_1 state to these higher triplet states. The unphysically low SOC constant values for the In complex should

be due to the utilization of the effective core potential. The Kohn–Sham frontier orbital distributions (Figure 4d) indicate that the S_1 state is attributable to the locally excited (LE) π – π^* state (HOMO–LUMO transition), while the T_2 and T_4 states consist of intraligand charge transfer (CT) states. For the CT-type T_2 and T_4 states, the hole and electron are located mainly on the Dipp units (electron donors) and the central N_2C_3 moiety (electron acceptor), respectively. The twisted conformations between donor and acceptors (dihedral angle: *ca.* 50° for CCCC, *ca.* 80° for CCNC) could result in the large SOC constant for S_1 – T_2 and S_1 – T_4 transitions because the large change in the orbital angular momentum could assist the electron–spin flipping.³⁸

The T_1 state of all complexes are assigned to the LE state (HOMO–LUMO transition), leading to the relatively small ζ values between their T_1 – S_0 transition.³⁹ Therefore, the observed average phosphorescence lifetimes at 77 K were over several tens of milliseconds (Table 3), especially reached over 300 ms in the case of **LAICl**. Such potentially long-lived triplet states could be used for further triplet-harvesting applications, although their phosphorescence has been quenched nonradiatively at room temperature so far.

As the packing structures of the complexes were almost identical, the quenching of the luminescence involving both fluorescence and phosphorescence of **LInCl** in the crystal at room temperature might be originated from the intrinsic nature of the complex. One of the possible reasons is the high activation energy for the intersystem crossing from S_1 to the triplet state.

The most singlet excitons of the indium complex could gain enough thermal energy required for the spin flip at room temperature in the crystals. Consequently, the triplet excitons generated at room temperature might be quenched through nonradiative paths from the T_1 states, leading to its remarkably low Φ_{PL} in the crystals compared to the other element molecules (Table 4). Meanwhile the considerable amount of the excitons should be trapped in the S_1 state at 77 K, resulting in the dual emission at this temperature (Figure 3c).

3. Conclusion

DKI complexes of the group 13 elements, (DKI)MCl₂ (M = Al, Ga, In), were synthesized by using the π -conjugated DKI ligand with the sterically hindered diisopropylphenyl units at the imine N atoms. The obtained complexes, **LA**Cl and **LGa**Cl, showed clear crystallization-induced emission effect. In contrast, **LIn**Cl exhibits only weak emission in both solution and crystal at room temperature. It was revealed that the strong spin–orbit coupling derived from the heavy indium atom significantly affects the photophysical processes of the complex. Finally, solid-state luminescent complexes were obtained especially from aluminum and gallium complexes.

Acknowledgement

This work was partially supported by the Yashima Environment Technology Foundation (for K.T.) a Grant-in-Aid for Early-Career Scientists (for S.I., JSPS KAKENHI Grant Numbers 21K14673), for Scientific Research (B) (for K.T., JSPS KAKENHI Grant Number, 24K01570).

Conflicts of Interest

The authors declare no conflicts of interest.

5. References

- 1 K. A. Williams, A. J. Boydston and C. W. Bielawski, *Chem. Soc. Rev.*, 2007, **36**, 729–744.
- 2 A. Wakamiya and S. Yamaguchi, *Bull. Chem. Soc. Jpn.*, 2015, **88**, 1357–1377.
- 3 F. Vidal and F. Jäkle, *Angew. Chem. Int. Ed.*, 2019, **58**, 5846–5870.
- 4 H. Helten, *Chem. Asian J.*, 2019, **14**, 919–935.
- 5 Y. Chujo and K. Tanaka, *Bull. Chem. Soc. Jpn.*, 2015, **88**, 633–643.
- 6 M. Gon, K. Tanaka and Y. Chujo, *Polym. J.*, 2018, **50**, 109–126.
- 7 K. Tanaka and Y. Chujo, *Polym. J.*, 2023, **55**, 353–364.
- 8 A. M. Priegert, B. W. Rawe, S. C. Serin and D. P. Gates, *Chem. Soc. Rev.*, 2015, **45**, 922–953.
- 9 A. Loudet and K. Burgess, *Chem. Rev.*, 2007, **107**, 4891–4932.
- 10 K. Tanaka, M. Gon, S. Ito, J. Ochi and Y. Chujo, *Coord. Chem. Rev.*, 2022, **472**, 214779.
- 11 H. E. Hackney and D. G. Hall, *ChemPhotoChem*, 2022, **6**, e202100219.
- 12 M. Mamada, M. Hayakawa, J. Ochi and T. Hatakeyama, *Chem. Soc. Rev.*, 2024, **53**, 1624–1692.
- 13 M. Gon, S. Ito, K. Tanaka and Y. Chujo, *Bull. Chem. Soc. Jpn.*, 2021, **94**, 2290–2301.
- 14 H. Sun, X. Guo and A. Facchetti, *Chem*, 2020, **6**, 1310–1326.
- 15 C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913–915.
- 16 P. E. Burrows, L. S. Sapochak, D. M. McCarty, S. R. Forrest and M. E. Thompson, *Appl. Phys. Lett.*, 1994, **64**, 2718–2720.
- 17 S. Kusaka, R. Sakamoto and H. Nishihara, *Inorg. Chem.*, 2014, **53**, 3275–3277.
- 18 A. Sumiyoshi, Y. Chiba, R. Matsuoka, T. Noda and T. Nabeshima, *Dalton Trans.*, 2019, **48**, 13169–13175.

- 19 W. Schorn, D. Grosse-Hagenbrock, B. Oelkers and J. Sundermeyer, *Dalton Trans.*, 2016, **45**, 1201–1207.
- 20 S. Ito, M. Hashizume, H. Taka, H. Kita, K. Tanaka and Y. Chujo, *Mater. Chem. Front.*, 2023, **7**, 4971–4983.
- 21 Y. Aoyama, Y. Sakai, S. Ito and K. Tanaka, *Chem. Eur. J.*, 2023, **29**, e202300654.
- 22 F. P. Macedo, C. Gwengo, S. V. Lindeman, M. D. Smith and J. R. Gardinier, *Eur. J. Inorg. Chem.*, 2008, **2008**, 3200–3211.
- 23 R. Yoshii, A. Hirose, K. Tanaka and Y. Chujo, *Chem. Eur. J.*, 2014, **20**, 8320–8324.
- 24 R. Yoshii, A. Hirose, K. Tanaka and Y. Chujo, *J. Am. Chem. Soc.*, 2014, **136**, 18131–18139.
- 25 S. Ito, K. Tanaka and Y. Chujo, *Inorganics*, 2019, **7**, 100.
- 26 M. Yamaguchi, S. Ito, A. Hirose, K. Tanaka and Y. Chujo, *Mater. Chem. Front.*, 2017, **1**, 1573–1579.
- 27 S. Ito, A. Hirose, M. Yamaguchi, K. Tanaka and Y. Chujo, *J. Mater. Chem. C*, 2016, **4**, 5564–5571.
- 28 S. Ito, M. Yaegashi, K. Tanaka and Y. Chujo, *Chem. Eur. J.*, 2021, **27**, 9302–9312.
- 29 M. Yamaguchi, S. Ito, A. Hirose, K. Tanaka and Y. Chujo, *J. Mater. Chem. C*, 2016, **4**, 5314–5319.
- 30 C. Chen, S. M. Bellows and P. L. Holland, *Dalton Trans.*, 2015, **44**, 16654–16670.
- 31 M. Arrowsmith, M. R. Crimmin, M. S. Hill and G. Kociok-Köhn, *Dalton Trans.*, 2013, **42**, 9720–9726.
- 32 M. Stender, B. Eichler, N. Hardman, P. Power, J. Prust, M. Noltemeyer and H. Roesky, *Inorg. Chem.*, 2001, **40**, 2794–9.
- 33 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G.

Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16 Rev. C.01*, Wallingford, CT, 2016.

34 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

35 B. Metz, H. Stoll and M. Dolg, *J. Chem. Phys.*, 2000, **113**, 2563–2569.

36 M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, Eds., *Handbook of Photochemistry*, CRC Press, Boca Raton, 3rd Ed., 2019.

37 E. Epifanovsky, A. T. B. Gilbert, X. Feng, J. Lee, Y. Mao, N. Mardirossian, P. Pokhilko, A. F. White, M. P. Coons, A. L. Dempwolff, Z. Gan, D. Hait, P. R. Horn, L. D. Jacobson, I. Kaliman, J. Kussmann, A. W. Lange, K. U. Lao, D. S. Levine, J. Liu, S. C. McKenzie, A. F. Morrison, K. D. Nanda, F. Plasser, D. R. Rehn, M. L. Vidal, Z.-Q. You, Y. Zhu, B. Alam, B. J. Albrecht, A. Aldossary, E. Alguire, J. H. Andersen, V. Athavale, D. Barton, K. Begam, A. Behn, N. Bellonzi, Y. A. Bernard, E. J. Berquist, H. G. A. Burton, A. Carreras, K. Carter-Fenk, R. Chakraborty, A. D. Chien, K. D. Closser, V. Cofer-Shabica, S. Dasgupta, M. de Wergifosse, J. Deng, M. Didenhofen, H. Do, S. Ehlert, P.-T. Fang, S. Fatehi, Q. Feng, T. Friedhoff, J. Gayvert, Q. Ge, G. Gidofalvi, M. Goldey, J. Gomes, C. E. González-Espinoza, S. Gulania, A. O. Gunina, M. W. D. Hanson-Heine, P. H. P. Harbach, A. Hauser, M. F. Herbst, M. H. Vera, M. Hodecker, Z. C. Holden, S. Houck, X. Huang, K. Hui, B. C. Huynh, M. Ivanov, Á. Jász, H. Ji, H. Jiang, B. Kaduk, S. Kähler, K. Khistyayev, J. Kim, G. Kis, P. Klunzinger, Z. Koczor-Benda, J. H. Koh, D. Kosenkov, L. Koulias, T. Kowalczyk, C. M. Krauter, K. Kue, A. Kunitsa, T. Kus, I. Ladjanski, A. Landau, K. V. Lawler, D. Lefrancois, S. Lehtola, R. R. Li, Y.-P. Li, J. Liang, M. Liebenthal, H.-H. Lin, Y.-S. Lin, F. Liu, K.-Y. Liu, M. Loipersberger, A. Luenser, A. Manjanath, P. Manohar, E. Mansoor, S. F. Manzer, S.-P. Mao, A. V. Marenich, T. Markovich, S. Mason, S. A. Maurer, P. F. McLaughlin, M. F. S. J. Menger, J.-M. Mewes, S. A. Mewes, P. Morgante, J. W. Mullinax, K. J. Oosterbaan, G. Paran, A. C. Paul, S. K. Paul, F. Pavošević, Z. Pei, S. Prager, E. I. Proynov, Á. Rák, E. Ramos-Cordoba, B. Rana, A. E. Rask, A. Rettig, R. M. Richard, F. Rob, E. Rossomme, T. Scheele, M. Scheurer, M. Schneider, N. Sergueev, S. M. Sharada, W. Skomorowski, D. W. Small, C. J. Stein, Y.-C. Su, E. J. Sundstrom, Z. Tao, J. Thirman, G. J. Tornai, T. Tsuchimochi, N. M. Tubman, S. P. Veccham, O. Vydrov, J. Wenzel, J. Witte, A. Yamada, K. Yao, S. Yeganeh, S. R. Yost, A. Zech, I. Y. Zhang, X. Zhang, Y. Zhang, D. Zuev, A. Aspuru-Guzik, A. T. Bell, N. A. Besley, K. B. Bravaya, B. R. Brooks, D. Casanova,

J.-D. Chai, S. Coriani, C. J. Cramer, G. Cserey, A. E. DePrince, R. A. DiStasio, A. Dreuw, B. D. Dunietz, T. R. Furlani, W. A. Goddard, S. Hammes-Schiffer, T. Head-Gordon, W. J. Hehre, C.-P. Hsu, T.-C. Jagau, Y. Jung, A. Klamt, J. Kong, D. S. Lambrecht, W. Liang, N. J. Mayhall, C. W. McCurdy, J. B. Neaton, C. Ochsenfeld, J. A. Parkhill, R. Peverati, V. A. Rassolov, Y. Shao, L. V. Slipchenko, T. Stauch, R. P. Steele, J. E. Subotnik, A. J. W. Thom, A. Tkatchenko, D. G. Truhlar, T. V. Voorhis, T. A. Wesolowski, K. B. Whaley, H. L. Woodcock, P. M. Zimmerman, S. Faraji, P. M. W. Gill, M. Head-Gordon, J. M. Herbert and A. I. Krylov, *J. Chem. Phys.*, 2021, **155**, 084801.

38 W. Shao and J. Kim, *Acc. Chem. Res.*, 2022, **55**, 1573–1585.

39 Y. Su, M. Wu, G. Wang, J. Li, X. Chen, X. Li, G. Wang and K. Zhang, *Chem. Commun.*, 2023, **59**, 1525–1528.