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# Regulating the photoluminescence of aluminium complexes from nonluminescence to room-temperature phosphorescence by tuning the metal substituents

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Although luminescent aluminum compounds have been utilized for emitting and electron transporting layers in organic light-emitting diodes, most of them often exhibit not phosphorescence but fluorescence with lower photoluminescent quantum yields in the aggregated state than those in the amorphous state due to concentration quenching. Here we show the synthesis and optical properties of  $\beta$ -diketiminate aluminum complexes, such as crystallization-induced emission (CIE) and room-temperature phosphorescence (RTP), and the substituent effects of the central element. The dihaloaluminum complexes were found to exhibit the CIE property, especially RTP from the diiodo complex, while the dialkyl ones showed almost no emission in both solution and solid states. Theoretical calculations suggested that undesired structural relaxation in the singlet excited state of dialkyl complexes should be suppressed by introducing electronegative halogens instead of alkyl groups. Our findings could provide a molecular design not only for obtaining luminescent complexes but also for achieving triplet-harvesting materials.

Aluminum complexes have been utilized as a Lewis acid in organic reactions and polymerizations and as a platform for constructing optoelectronic materials. In particular, luminescent aluminum complexes have been widely investigated since organic light-emitting diodes (OLEDs) were fabricated with tris(8-quinolinolato)aluminum (Alq<sub>3</sub>) as an emitting layer<sup>1-3</sup>. Their luminescence color can be tuned over whole visible region by modifying the electronic structure of their ligand moieties, especially in the case of 8-quinolinolate<sup>4</sup> and salen<sup>5</sup> complexes. However, most of these complexes exhibit only fluorescence rather than phosphorescence and critically weaker emission intensity in the solid state than that in the dilute solution state although they are required to show luminescent properties in the condensed state for the device applications. In addition, there are limited series of stable aluminum complexes which are able to exhibit remarkable emission properties<sup>2,6</sup>. Thus, it is still of great significance to explore a class of solid-state luminescent aluminum complexes, especially with room-temperature phosphorescence (RTP).

 $\beta$ -Diketiminate ligands are characterized by the two sp<sup>2</sup>-nitrogen atoms as the coordination centers. Compared to the corresponding acetylacetonate ligands, their steric and electronic demands are able to be easily tuned by the substituents on the nitrogen atoms as well as the carbon atoms. Therefore, these ligands have enabled to isolate reactive aluminum(I) species<sup>7</sup>, which have paved the way for accessing various fruitful chemical transformations, like inert-bond activations<sup>8-11</sup>. Furthermore, the series of the four-coordinated complexes of the group 13 elements have been synthesized by using those ligands<sup>12,13</sup>. Despite tremendous research efforts, the optical and/or electronic properties of aluminum(III) complexes with  $\beta$ diketiminate ligands have not been mainly focused on probably because they have very weak absorption bands in the visible region due to the limited  $\pi$ -conjugation length within the  $\beta$ -diketiminate ligands. On the other hand, it has been reported that the  $\beta$ -diketiminate complexes of the group 13 elements exhibit solid-state emission<sup>14-22</sup>. These reports have shown that the  $\pi$ -conjugation system of the  $\beta$ -diketiminate ligands should extend within the whole ligand and lead to the efficient luminescence. Importantly, the

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luminescence efficiency of those complexes in the crystalline states is typically higher than those in the dilute solutions and amorphous solids. This phenomenon is called crystallization-induced emission (CIE) and is beneficial because those luminophores are potentially applied for OLEDs, chemo-sensors, bioimaging, and laser amplifiers<sup>23-25</sup>. The bulky peripheral aromatic groups of the  $\beta$ -diketiminate ligands could be probably responsible for the fast non-radiative decay processes in solution<sup>26</sup> and prohibit  $\pi$ stacking which leads to critical concentration quenching in the solid state<sup>24</sup>. Hence, these complexes could open up an avenue for achieving functional optical materials with solid-state luminescent properties based on aluminum<sup>27-34</sup>. Herein, we envisioned that a class of the  $\pi$ -extended  $\beta$ -diketiminate ligand serves as a scaffold to obtain efficient solid-state emission properties from aluminum complexes. Furthermore, aluminum allowed us to systematically evaluate the substituent effects at the central element on photophysical properties thanks to the easier access to aluminum complexes with different substituents than the other group 13 elements. As a result, it was demonstrated that dialkylaluminum and dihaloaluminum complexes are non-emissive and emissive, respectively, in crystalline states at room temperature. Theoretical calculations suggest that the alkyl substituents should lead to a significant structural relaxation at the excited state, which results in fast non-radiative quenching processes. Importantly, solid-state luminescent aluminum complexes were developed, especially the diiodoaluminum complex that exhibits efficient RTP with 0.54 of quantum yield.

# Results and discussion

# Synthesis and characterization

To assess the effects of substituents on aluminum on the photophysical properties of  $\beta$ -diketiminate complexes, we synthesized five compounds with different substituents (Fig. 1a). The isopropyl groups on the aromatic groups of the ligand (**LH**) were employed for the kinetic stabilization of the complex<sup>7,35–37</sup>. The dialkylaluminum complexes, **LAIMe** and **LAIEt**, were successfully synthesized by reacting trialkylaluminum with **LH** in toluene at 100 °C according to the literatures on the syntheses of the related complexes<sup>35,38,39</sup>. The dialkolaluminum complexes, **LAICI**, **LAIBr**, and **LAII**, were synthesized with the modified procedure of the related compounds

through the reactions of **LH** and *n*-butyllithium followed by the treatment with the corresponding aluminum trihalides<sup>35,36</sup>. These molecular structures were characterized with <sup>1</sup>H, <sup>13</sup>C{1H} and <sup>27</sup>Al{<sup>1</sup>H} NMR spectroscopies, high-resolution mass (HRMS) spectrometry, elemental analysis, and single-crystal X-ray diffraction analysis (Fig. 1b–e).

#### Photophysical properties at room temperature

There are two significant effects from the substituents on the photoluminescent properties (Fig. 2a): (i) the dihaloaluminum complexes emit light in solid states at room temperature, while the dialkyl ones hardly show emission under the same condition; (ii) the emission color of the dihaloaluminum complexes depends on the type of halogen (LAICl, blue; LAIBr, bluish white; LAII, green). Meanwhile, all compounds exhibited almost no luminescence in the solution states at room temperature in the similar manner as shown in the previous reports<sup>15–17,40</sup>. The previous studies demonstrated that the conventional  $\beta$ -diketiminate complexes have the CIE property with blue emission in crystalline states at room temperature when neither electron-accepting nor donating substituent was introduced on the ligands. Therefore, the non-emissive nature of the alkylaluminum complexes and the halogen-dependent emission color are the peculiar features among this class of luminophores.

We conducted spectroscopic studies under nitrogen at room temperature to elucidate the electronic structures of the complexes (Fig. 2b–d and Table 1). First, UV–vis absorption spectra were recorded in the 2-methylpentane (2MP)/toluene solutions (99/1, v/v,  $1 \times 10^{-5}$  M) at room temperature (Fig. 2b). All compounds showed similar absorption spectra with slight difference in the position of absorption maximum. The shapes and positions of the longest-wavelength absorption bands were similar to the typical  $\beta$ -diketiminate complexes and assignable mainly to the  $\pi$ – $\pi$ \* (S<sub>0</sub>–S<sub>1</sub>) transition of the ligand moiety, suggesting that the electronic character of the ground-state structure of the complexes should not be affected by the substituents on the aluminum atom. Nevertheless, the substituents apparently change the S<sub>0</sub>–S<sub>1</sub> transition energy probably due to their different contribution to the frontier orbitals<sup>41</sup>. Second, photoluminescent (PL) spectra were measured for the same solutions and their crystalline powders (Fig. 2c, d). As we presumed, quite weak and broad



Fig. 1 | Aluminum complexes investigated in this study. a Synthetic scheme of the dialkylaluminum and dihaloaluminum complexes. Single-crystal structures of b LAIMe, c LAICI, d LAIBr, and e LAII.



Fig. 2 | Photophysical properties of aluminum  $\beta$ -diketiminate complexes. a Photographic images of solutions and crystals of the complexes. UV, 365 nm. b, c UV-vis absorption and PL spectra in solutions at room temperature, respectively. d PL spectra in crystalline states at room temperature. e, f PL spectra in

solutions and crystalline states at 77 K, respectively. **g**, **h** Phosphorescence decay curve of **LAIBr** (detected at 511 nm) and **LAII** (detected at 515 nm) in crystalline states at room temperature, respectively. Solid lines represent fitting curves.

values were determined to be 0.48 for LAICI, 0.44 for LAIBr, and 0.58 for

LAII. Importantly, the PL spectra of LAIBr and LAII composed two distinct

bands in the blue and green regions. PL lifetime ( $\tau_{\rm PL}$ ) measurements

revealed that the shorter-wavelength bands possessed nanosecond-order  $\tau_{PL}$ , while the longer-wavelength ones had microsecond-order  $\tau_{PL}$  (Fig. 2g, h

and Table 2). Finally, their PL spectra recorded after several milliseconds

after photoexcitation showed only longer-wavelength component (Supplementary Fig. 1). Consequently, the blue- and green-emission bands were assignable to fluorescence and phosphorescence, respectively. These data mean that the heavy atom effect of bromine and iodine should lead to the RTP properties of **LAIBr** and **LAII**. The estimated phosphorescence quantum yield ( $\Phi_P$ ) value of **LAII** (0.54) is the highest one among the aluminum complexes. It is also of interest to note that the related boron complexes with iodine on the peripheral aromatic rings hardly show apparent RTP<sup>18</sup>. The heavy atoms directly attached on the central element might efficiently accelerate intersystem crossing and phosphorescence

From the fluorescence and phosphorescence quantum yields and PL

each rate constant. For all three complexes in the solution states, quite large

emission spectra were obtained from all solutions. Their absolute quantum yields ( $\Phi_{\rm PL}$ ) were lower than 0.01. In the crystalline state, LAIMe and LAIEt hardly exhibited emission enhancement ( $\Phi_{\rm PL} < 0.01$ ), while LAICI, LAIBr, and LAII showed significant emission spectra in the visible region.  $\Phi_{\rm PL}$ 

# Table 1 | Results of photophysical measurements at room temperature<sup>a</sup>

		λ <sub>abs</sub> / nm	ε/ 10⁴ M⁻¹ cm⁻¹	λ <sub>Fluo</sub> / nm	λ <sub>Phos</sub> / nm	$\Phi_{F}$	Φ <sub>P</sub>
LAIMe	Solution	403	2.5	460	n.d.	<0.01	-
	Crystal	-	-	473	n.d.	<0.01	-
LAIEt	Solution	410	2.0	458	n.d.	<0.01	-
	Crystal	-	-	480	n.d.	<0.01	-
LAICI	Solution	386	2.8	436	n.d.	<0.01	<0.01
	Crystal	-	-	442	n.d.	0.48	-
LAIBr	Solution	385	2.9	441	n.d.	<0.01	<0.01
	Crystal	-	-	447	511	0.25	0.19
LAII	Solution	384	2.4	450	528	<0.01	<0.01
	Crystal	-	-	454	515	0.04	0.54

"Photoluminescence properties were recorded with photoexcitation at the absorption maximum wavelength in the solution state at room temperature. Solution, 1 × 10<sup>-5</sup> M in 2-methylpentane/ toluene (99/1, v/v); crystal, recrystallized from hexane; –, not determined. Phosphorescence spectra were recorded with pulsed excitation. Quantum yields of fluorescence and phosphorescence were estimated by absolute quantum yields and deconvoluted photoluminescence spectra with multicomponent Gaussian functions. processes.

Table 2 | PL lifetime and estimated rate constants at room temperature<sup>a</sup>

		<τ <sub>F</sub> >/ns	<τ <sub>P</sub> >/ms	<i>k</i> <sub>r</sub> <sup>s</sup> /10 <sup>7</sup> s <sup>−1</sup>	<i>k</i> <sub>nr</sub> <sup>s</sup> /10 <sup>7</sup> s <sup>-1</sup>	<i>k</i> <sub>ISC</sub> <sup>S</sup> /10 <sup>7</sup> s <sup>-1</sup>	$k_{\rm r}^{\rm T}/10^2{\rm s}^{-1}$	$k_{nr}^{T}/10^{2} s^{-1}$
LAICI	Solution	<0.03	-	>3.3	>3300	>3.3	-	-
	Crystal	2.1	-	34	31	6.4	-	-
LAIBr	Solution	<0.04	-	>2.5	>2500	>25	-	-
	Crystal	2.0	4.0	13	16	23	1.1	1.4
LAII	Solution	<0.04	0.10	>1.0	>2200	>250	0.4	100
	Crystal	0.14	0.29	29	10	680	20	15

 $^{a}$ < $\tau_{P}$ > and < $\tau_{P}$ >, average fluorescence and phosphorescence lifetimes, respectively;  $k_r^s$ , radiative decay rate constant from singlet state (fluorescence);  $k_{nr}^s$ , non-radiative decay rate constant from singlet state (internal conversion);  $k_{ISC}^s$ , intersystem crossing rate constant from singlet state;  $k_r^T$ , radiative decay rate constant from triplet state (phosphorescence);  $k_{nr}^T$ , non-radiative decay rate constant from triplet state. ( $r_{P}$ > values for solutions are upper limits estimated by the streak camera system.  $k_r^s$ ,  $k_{nr}^s$ , and  $k_{ISC}^s$  values for solutions are lower limits calculated from the upper limit of the < $\tau_{P}$ > values.

# Table 3 | Results of photoluminescence measurements at 77 K<sup>a</sup>

		λ <sub>Fluo</sub> /nm	$\lambda_{Phos}/nm$	$\phi_{Fluo}$	$\phi_{Phos}$
LAIMe	Solution	445	541	0.96	0.04
	Crystal	474	569	0.25	n.d.
LAIEt	Solution	429	530	n.d.	n.d.
	Crystal	429	n.d.	n.d.	n.d.
LAICI	Solution	428	510	0.93	0.03
	Crystal	422	535	0.96	0.04
LAIBr	Solution	435	514	0.56	0.35
	Crystal	422	506	0.56	0.26
LAII	Solution	426	515	0.13	0.33
	Crystal	425	507	0.03	0.74

<sup>a</sup>Excited at the absorption maximum wavelength in solution state at room temperature. Solution,  $1 \times 10^{-5}$  M in 2-methylpentane/toluene (99/1, v/v); crystal, recrystallized from hexane; n.d., not determined due to negligible phosphorescence. Phosphorescence spectra were recorded with pulsed excitation. Quantum yields of fluorescence and phosphorescence were estimated by absolute quantum yields and deconvoluted photoluminescence spectra with multi-component Gaussian functions.

non-radiative decay rate constants for singlet states  $(k_{nr}^{s} \sim 10^{10} s^{-1})$  were obtained, suggesting that most excited molecules would be quenched nonradiatively through the internal conversion from S<sub>1</sub> to S<sub>0</sub> probably because this process could occur through conical intersections<sup>26</sup>. Only in the case of LAII, the rapid intersystem crossing process derived from the strong heavy atom effect of iodine could occur to some extent  $(k_{ISC}/k_{nr}^{s} \sim 0.1)$ . On the other hand, the crystals of these complexes exhibited at least 100 times smaller  $k_{nr}^{s}$  values than their solutions, leading to their CIE properties. In the cases of LAIBr and LAII, the suppression of the internal conversion should open the intersystem crossing processes as well as fluorescence. It is worth noting that the radiative rate constant from singlet states  $(k_{r}^{s})$  and  $k_{ISC}^{s}$  of some complexes were enhanced by the crystallization, which might originate from the intermolecular interactions and could contribute to their CIE properties.

#### Photophysical properties at 77 K

To gain further information about the photophysical processes, we recorded PL spectra of the solutions and crystalline powders at 77 K with a cryostat under nitrogen atmosphere (Fig. 2e and Table 3). Importantly, all compounds clearly exhibited phosphorescence in the frozen solution state, probably because the non-radiative decay processes could be closed at the low temperature. Indeed, the hypsochromic shifts of the emission band were observed, indicating that structural changes in the excited state should be hampered under the frozen environment. In other words, it is suggested that there are significant structural relaxations in the excited state that cause non-radiative decay of the singlet excited states in room-temperature solutions. Interestingly, LAIMe and LAICI exhibited phosphorescence at 77 K, despite the absence of heavy atoms, implying the intrinsic triplet-forming properties

of these series of compounds<sup>40</sup>. In the crystalline states at 77 K, the slight hypsochromic shifts of emission bands were observed except for **LAIMe**. These shifts might originate from the tight packing of the crystals. On the other hand, the bathochromic shift for the crystal of **LAIMe** might be attributed to the weakening of the 0–0 band. Significantly, the apparent crystallization-induced phosphorescence enhancement was observed from **LAII**. The estimated  $\Phi_{\text{Phos}}$  in crystal was 2.2 times higher than that in the frozen solution, possibly because of the acceleration of intersystem crossing and phosphorescence processes and because the restriction of non-radiative decay from excited triplet states.

#### Theoretical calculations

Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed with the Gaussian 16 package<sup>42</sup> to study the electronic structures of the dimethylaluminum and dihaloaluminum complexes (Fig. 3). Geometry optimization was performed for both S<sub>0</sub> and S1 states with the CAM-B3LYP functional and the Lanl2DZ basis set for I and the 6-31G(d,p) one for the other atoms, followed by single-point transition energy calculations at the same level of theory except for the basis set for the light atoms (6-311++G(d,p)). The significant structural relaxation at the S1 state was estimated only for LAIMe, leading to the narrow  $S_0$ - $S_1$  energy gap (1.58 eV) and the small oscillator strength (f=0.0080). The most characteristic change in the relaxation was the elongation of one of the Al–C bonds from 1.98 Å ( $S_0$ ) to 2.30 Å ( $S_1$ ). At the  $S_0$ geometry, its Kohn-Sham highest occupied molecular orbital (HOMO) was significantly delocalized over the Al-C bond as well as the ligand moiety, while the Kohn-Sham lowest unoccupied molecular orbital (LUMO) possessed little contribution from this bond because of a nodal plane passing through it (Supplementary Tables 15 and 16). Hence, the electron density between aluminum and carbon atoms should decrease upon the photoexcitation from S<sub>0</sub> to S<sub>1</sub>, resulting in the weakening of the bond and the considerably large structural relaxation at the S1 state. Similar photoinduced bond weakening or activation of Al-C bond have been reported in other systems of photochemical reactions<sup>43-46</sup>. For the resulted S<sub>1</sub> geometry, the HOMO mainly located at the Al-C moiety, where the HOMO-LUMO overlap much less effectively than that for the S<sub>0</sub> geometry, making the f value of the  $S_1$ - $S_0$  transition smaller. Therefore, it is suggested that the structural relaxation should be responsible for the non-radiative decay process of the dialkylaluminum complexes.

On the other hand, the dihaloaluminum complexes presented only smaller structural changes between the S<sub>0</sub> and S<sub>1</sub> states, probably because the contribution from the Al–halogen bond to their HOMO would be smaller (Supplementary Table 17). Natural bond orbital (NBO) analysis suggested that the orbital on the Al–C bond should be mainly composed of the NBO attributed to the 2*p* orbital of the carbon atom, which is located at the similar energy region with the HOMO of the  $\beta$ -diketiminate ligand (Supplementary Tables 20 and 21). As the corresponding *p* orbitals of chlorine, bromine, and iodine should be located at the much lower energy region because of their large electronegativity than carbon (Supplementary Tables 22 and 23), the Al–halogen bond would not strongly contribute to the HOMO of the



**Fig. 3** | **Results of (TD-)DFT calculations. a** Calculated energies of Kohn–Sham HOMO and NBO of the corresponding Al-X (X = Me, Cl, Br, and I) bond. **b**, **c** Optimized geometries and energies of **LAICI** and **LAIMe**, respectively, at S<sub>0</sub> and

 $S_1$  states. **d** Kohn–Sham HOMO, LUMO, and NBO. Orange circles highlight the contribution from the substituent on aluminum to each HOMO.

dihaloaluminum complexes due to the weaker orbital interactions. As a result, the undesired structural relaxation causing the non-radiative quenching could hardly occur in the S<sub>1</sub> state and the S<sub>1</sub>–S<sub>0</sub> electronic transition would be no longer forbidden at its S<sub>1</sub> geometry (e.g., f = 0.5070 for **LAICI**, Fig. 3b). Consequently, it is suggested that the photophysical processes of  $\beta$ -diketiminate complexes could be drastically modulated by the substituents on the central element. In addition, it is worth noting that the electron-donating contribution from the Al–C bond destabilizes the HOMO level compared to the dihaloaluminum complexes, leading to the lower S<sub>1</sub> state consistent with the observed redshift of the absorption band. Indeed, **LAIEt**, with the more strongly electron-donating ethyl group, showed the absorption band in the lowest energy region among the complexes. The stronger electron-donating ability of the ethyl groups might be responsible for the non-emissive behavior of **LAIEt** even in the solution at 77 K (see Supplementary Note 2).

We also calculated excited triplet state  $(T_n)$  energy and spin–orbit coupling (SOC) constants between  $S_m$  and  $T_n$  states,  $\xi(S_m - T_n)$ , for the dihaloaluminum complexes with the Q-Chem 5 package<sup>47</sup> to get deeper insights into their phosphorescent properties (Fig. 4). The S<sub>1</sub> and T<sub>1</sub> states of each complex were dominantly characterized by the locally excited (LE) state within the central N<sub>2</sub>C<sub>3</sub> moiety. As the S<sub>1</sub>–T<sub>1</sub> energy gap was calculated to be about 1.0 eV or larger, the ISC from S<sub>1</sub> to T<sub>1</sub> seemed to be less efficient. On the other hand, the T<sub>n</sub> (n = 2-4) states were located in the similar energy region of the S<sub>1</sub> state (±100 meV). In addition, the SOC values were estimated to be large enough to accept the efficient ISC between S<sub>1</sub> and T<sub>n</sub>. For LAICI and LAIBr, these large SOC values are attributable to the intraligand charge transfer (CT) character of these  $T_n$  states with twisted conformations between the donor (aromatic rings) and acceptor (N<sub>2</sub>C<sub>3</sub> unit) as shown in Fig. 4b. As the transitions between the  $S_1(LE)$  to the  $T_n(CT)$  occurs with the large change in orbital angular momentum derived from the twisted conformations, the electron-spin flipping is allowed with holding the angular momentum conservation<sup>48</sup>. On the other hand, the T<sub>2</sub> and T<sub>3</sub> states of LAII significantly consist of the transition from the nonbonding orbitals (lone pairs) of the iodine atoms (HOMO-1 and HOMO-2) to its LUMO. Consequently, the heavy atom effect of iodine could efficiently accelerate the ISC between  $S_1$  to  $T_2$  and  $T_3$ . Considered the absence of RTP from the difluoroboron complexes with iodinated  $\beta$ -diketiminate ligands<sup>18</sup>, the heavy atoms directly attached to the central atom should be responsible for the efficient RTP property. Importantly, it was suggested that the SOC constants not only between S1 and Tn but also between S0 and T1 significantly increased as the atomic number of the halogen atoms become larger because of the heavy atom effect. Therefore, both of ISC and phosphorescence processes should be enhanced in LAIBr and LAII compared to LAICI.

### Conclusion

CIE-active four-coordinated  $\beta$ -diketiminate aluminum(III) complexes, LAICI, LAIBr, and LAII were discovered. From the spectroscopic measurements and the theoretical calculations, it was strongly suggested that the 2p orbital of the carbon atom in LAIMe significantly contributed to its HOMO and induced the undesirable structural relaxation in the S<sub>1</sub> state. As a result of the relaxation, internal conversion from S<sub>1</sub> to S<sub>0</sub> should occur even in the crystalline state at room temperature. The series of NBO analysis



Fig. 4 | Excited singlet and triplet states of the complexes. a Excitation energies of singlet and triplet states relative to each  $S_0$  state. Orbital contributions to each state and SOC constants between  $S_m$  and  $T_n$  states are shown in gray texts. H and L denote HOMO and LUMO. **b** Kohn–Sham molecular orbital distributions (isovalue = 0.03).

certainly proposed that more electronegative halogen substituents would not disturb the HOMO distribution of the  $\beta$ -diketiminate moiety, leading to suppression of the non-radiative quenching paths. Thus, the dihaloaluminum complexes exhibited efficient photoluminescence in the crystalline state at room temperature. In particular, **LAII** exhibited RTP with 0.54 of the phosphorescence quantum yield as a result of the efficient heavy atom effect of iodine on the central element. Our strategy for constructing desired luminophores by modifying the substituents on the central element could be applicable not only for achieving further luminescent metal complexes but also for obtaining optoelectronic materials, reagents, and catalysts.

#### Methods

#### Characterization

<sup>1</sup>H (400 MHz) and <sup>13</sup>C{<sup>1</sup>H} (100 MHz) NMR spectra were recorded on a JEOL JNM-AL400 spectrometer. In <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, tetramethylsilane (TMS) and/or residual solvent peaks were used as an internal standard. <sup>27</sup>Al{<sup>1</sup>H} NMR (130 MHz) spectra were recorded on a JEOL JNM-ECZ500 spectrometer and referenced to 1.1 M Al(NO<sub>3</sub>)<sub>3</sub> in D<sub>2</sub>O (0 ppm) as an external standard. The peak in <sup>27</sup>Al{<sup>1</sup>H} NMR spectra at around 60 ppm was attributed to the signal from an NMR tube. HRMS was performed at the Technical Support Office (Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University), and the HRMS spectra were obtained on a Thermo Fisher Scientific EXACTIVE spectrometer for electrospray ionization (ESI) and for direct analysis in real time (DART). Single-crystal X-ray diffraction data were collected using a Rigaku R-AXIS RAPID-F. Data were collected at 93 K with graphitemonochromated Mo K $\alpha$  radiation diffractometer and an imaging plate. Equivalent reflections were merged, and a symmetry related absorption correction was carried out with the program ABSCOR<sup>49</sup>. The structures were solved with SHELXT 2014<sup>50</sup> and refined on  $F^2$  with SHELXL<sup>51</sup> on Yadokari-XG<sup>52</sup> or ShelXle<sup>53</sup>. The program ORTEP-3<sup>54</sup> was used to generate the X-ray structural diagram. For crystallographic data, see Supplementary Table 1. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

#### **Photophysical measurements**

UV-vis absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. Fluorescence and phosphorescence emission spectra and phosphorescence decay were measured with a HORIBA JOBIN YVON Fluorolog-3 spectrofluorometer and an Oxford Optistat DN for temperature control. Absolute photoluminescence quantum yields were measured with a Hamamatsu Photonics Quantaurus-QY Plus C13534-01 and a sample holder for low temperature, A11238-05, was used for the measurements at 77 K. Picosecond photoluminescence (PL) lifetimes were measured with the second harmonic generation of a Ti:sapphire pulsed laser (wavelength: 400 nm, pulse width: 100 fs, time resolution: 40 ps) and a streak camera (Hamamatsu Photonics C4334-01).

#### Materials

All reactions were performed under argon atmosphere using modified Schlenk line techniques and an MBRAUN glove box system, UNIlab, unless otherwise noted. Analytical thin layer chromatography was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with Wakogel C-200 SiO<sub>2</sub>. *n*-BuLi (1.55 M in hexane, Kanto Chemical Co., Inc), AlMe<sub>3</sub> (ca. 1.4 M in hexane, Tokyo Chemical Industry Co., Ltd.; TCI), AlEt<sub>3</sub> (ca. 1.0 M in hexane, TCI), AlBr<sub>3</sub> (99.999% trace metal basis, Sigma-Aldrich Co., LLC.; Aldrich), iodine (FUJIJILM Wako Pure Chemical Corporation; Wako), deoxygenated toluene (Wako), and deoxygenated hexane (Wako) were purchased from commercial sources and used as received. AlCl<sub>3</sub> (99.999% trace metal basis, Aldrich) was purified by sublimation under inert atmosphere before use. LH<sup>37</sup> and LAICl<sup>22</sup> were synthesized according to the reported literatures. LAIMe<sup>35</sup>, LAIBr<sup>36</sup>, and LAII<sup>36</sup> were synthesized by using modified procedures of the literature for the related compounds.

Synthesis of LAIMe. AlMe<sub>3</sub> (1.3 mL, ca. 1.4 M in hexane, 1.8 mmol) was added dropwise to a solution of LH (1.0 g, 1.8 mmol) in 5 mL of toluene at 0 °C. The yellow transparent solution was stirred at 0 °C for 5 min, allowed to warm to 100 °C, and stirred for 16 h. All volatiles were removed under reduced pressure. The crude product was dissolved in ca. 80 mL of hot hexane under air. After filtration with a warmed apparatus, the filtrate was slowly cooled to room temperature to give bright yellow crystals suitable for X-ray analysis (0.96 g, 87% yield). <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$ 7.14-7.00 (m, 10H), 6.82-6.79 (m, 6H), 5.72 (s, 1H), 3.57 (sept, 4H,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 1.35 (d, 12H,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ), 0.94 (d, 12H,  ${}^{3}J_{\text{H-H}} = 6.7 \text{ Hz}$ , -0.22 (s, 6H);  ${}^{13}\text{C}\{{}^{1}\text{H}\}$  NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  170.8 (C=N), 144.4, 141.3, 139.8, 129.2, 128.8, 127.6, 127.1, 124.5, 103.2, 28.6, 26.4, 23.9, -9.98; <sup>27</sup>Al{<sup>1</sup>H} NMR (130 MHz, C<sub>6</sub>D<sub>6</sub>): δ 148.4 (br); HRMS (ESI, m/z):  $[M + H]^+$  calcd. for  $C_{41}H_{51}AlN_2 + H^+$ , 599.3940; found, 599.3930; analysis (calcd., found for C41H51AlN2): C (82.23, 82.38), H (8.58, 8.43), N (4.68, 4.67).

**Synthesis of LAIEt.** AlEt<sub>3</sub> (0.92 mL, ca. 1.0 M in hexane, 0.92 mmol) was added dropwise to a solution of **LH** (0.5 g, 0.92 mmol) in 5 mL of toluene at room temperature. The yellow transparent solution was allowed to warm to 100 °C, and stirred for 16 h. After filtration with a pre-warmed glass filter, the filtrate was concentrated to give a crude crystal. The product was recrystallized from hexane under air to afford a pure compound as a bright yellow crystal (0.38 g, 65% yield). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.17–7.02 (m, 10H), 6.83–6.81 (m, 6H), 5.64 (s, 1H), 3.60 (sept, 4H, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz), 1.39 (d, 12H, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz), 1.37 (t, 6H, <sup>3</sup>J<sub>H-H</sub> = 8.3 Hz), 0.95 (d, 12H, <sup>3</sup>J<sub>H-H</sub> = 6.7 Hz), 0.34 (q, 4H, <sup>3</sup>J<sub>H-H</sub> = 8.1 Hz); HRMS (ESI, *m/z*): [M + H]<sup>+</sup> calcd. for C<sub>43</sub>H<sub>55</sub>AlN<sub>2</sub> + H<sup>+</sup>, 627.4253; found, 627.4260.

Synthesis of LAICI. To a slurry of LH (0.50 g, 0.91 mmol) and hexane (9 mL) was added n-BuLi (1.55 M in hexane, 0.65 mL, 1.0 mmol) dropwise at -78 °C. The mixture was stirred for 10 min at -78 °C, then allowed to slowly warm to r.t. and stirred for 5 h. The slurry was added to a suspension of freshly sublimed AlCl<sub>3</sub> (0.24 g, 1.82 mmol) in hexane (5 mL) at -78 °C. The mixture was warmed to 50 °C and stirred for 19 h at the same temperature. The product was extracted with hexane then filtered with Merck Millipore 0.20 µm hydrophobic PTFE filter repeatedly. The filtrate was concentrated under reduced pressure. Analytically pure product was obtained by repeated crystallization from hexane with slow evaporation method. The crystals were collected and washed with hexane to give the spectroscopically pure and X-ray quality product (87 mg, 18% yield). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): 8 7.08-6.99 (m, 10H), 6.81-6.74 (m, 6H, Ar), 5.84 (s, 1H), 3.65 (sept, 4H,  ${}^{3}J_{H-H} = 6.7$  Hz), 1.47 (d, 12H,  ${}^{3}J_{H-H} = 6.7$  Hz), 0.94 (d, 12H,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ );  ${}^{13}C{}^{1}H$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  172.2, 144.6, 138.1, 137.9, 129.5, 129.0, 127.7, 127.6, 124.4, 103.6, 28.7, 26.1, 23.6;  $^{27}$ Al{<sup>1</sup>H} NMR (130 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  100.7; HRMS (DART, *m/z*): [M + H]<sup>+</sup> calcd. for  $C_{39}H_{45}AlCl_2N_2 + H^+$ , 639.2848; found, 639.2828; analysis (calcd., found for C<sub>39</sub>H<sub>45</sub>AlCl<sub>2</sub>N<sub>2</sub>): C (73.23, 73.27), H (7.09, 7.19), N (4.38, 4.33), Cl (11.08, 10.78).

**Synthesis of LAIBr**. To a slurry of **LH** (0.50 g, 0.91 mmol) and hexane (9 mL) was added *n*-BuLi (1.55 M in hexane, 0.65 mL, 1.0 mmol) dropwise

at -78 °C. The mixture was stirred for 10 min at -78 °C, then allowed to slowly warm to r.t. and stirred for 5 h. The vellow slurry was concentrated under reduced pressure. The yellow powder was washed with hexane and dried under reduced pressure to give the solid of the lithium complex (0.50 mg, 99%). To a precooled solution of the lithium complex (0.29 g, 0.53 mmol) in toluene (6 mL) was added a suspension of AlBr<sub>3</sub> (0.14 g, 0.53 mmol) dropwise at -78 °C. The mixture was allowed to slowly warm to r.t. and stirred for 14 h. The turbid orange solution was filtered with a Merck Millipore 0.20 µm hydrophobic PTFE filter. The filtrate was concentrated under reduced pressure. Analytically pure product was obtained by repeated crystallization from mixed solvent of toluene and hexane (ca. 1/10, vol/vol). The crystals were collected and washed with hexane to give the spectroscopically pure and X-ray quality product (0.13 g, 33%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.08–7.00 (m, 10H), 6.79–6.73 (m, 6H), 5.90 (s, 1H), 3.72 (sept, 4H,  ${}^{3}J_{H-H} = 6.7$  Hz), 1.47 (d, 12H,  ${}^{3}J_{H-H} = 6.6$  Hz), 0.92 (d, 12H,  ${}^{3}J_{H-H} = 6.7 \text{ Hz}$ ;  ${}^{13}C{}^{1}H$  NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  172.7, 145.0, 138.9, 138.4, 129.6, 129.2, 128.3, 127.8, 124.9, 104.9, 29.2, 26.9, 23.8; HRMS  $(DART, m/z): [M + H]^+$  calcd. for  $C_{39}H_{45}AlBr_2N_2 + H^+$ , 727.1838; found, 727.1831; [M-Br]<sup>+</sup> calcd. for C<sub>39</sub>H<sub>45</sub>AlBrN<sub>2</sub><sup>+</sup>, 647.2576; found, 647.2570.

**Synthesis of LAII.** To a solution of **LAIMe** (1.5 g, 2.5 mmol) in toluene (65 mL) was added a solution of I<sub>2</sub> (1.6 g, 6.3 mmol) in toluene (14 mL) dropwise at 0 °C. The mixture was allowed to slowly warm to r.t. and stirred for 3 days. The dark red solution was filtered with a Merck Millipore 0.20 µm hydrophobic PTFE filter. The filtrate was concentrated under reduced pressure. Analytically pure product was obtained by repeated crystallization from mixed solvent of toluene and hexane. The yellow crystals were collected and washed with hexane to give the spectroscopically pure and X-ray quality product (0.82 g, 40% yield). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.08–7.00 (m, 10H), 6.77–6.75 (m, 6H), 6.02 (s, 1H), 3.78 (br, 4H), 1.47 (d, 12H, <sup>3</sup>J<sub>H-H</sub> = 6.6 Hz), 0.90 (br, 12H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  172.8, 145.1, 139.2, 138.5, 129.6, 129.1, 128.5, 128.4, 127.8, 125.0, 105.9, 29.5, 23.7; HRMS (DART, *m/z*): [M + H]<sup>+</sup> calcd. for C<sub>39</sub>H<sub>45</sub>AlI<sub>2</sub>N<sub>2</sub> + H<sup>+</sup>, 823.1544; found, 823.1560.

#### **Theoretical calculations**

All calculations were carried out using Gaussian 16 Revision C.03 at the (TD-)CAM-B3LYP/6-31G(d,p) and (TD-)CAM-B3LYP/6-311++G(d,p) levels of theory for geometry optimizations and for time-dependent singlepoint calculations, respectively. All optimized structures were confirmed to be at local minimum using frequency calculations. The crystal structures were employed as the initial geometries of the optimizations at S<sub>0</sub> states. The initial geometries for the optimization at S<sub>1</sub> states were the corresponding optimized structures at the S<sub>0</sub> states. Calculated low frequencies are listed in Supplementary Tables 7-14. Molecular orbital components which have large absolute values of orbital coefficients are shown in Supplementary Tables 15-18. Supplementary Table 19 shows the calculated frontier orbital energies and the electronic transitions for LAIMe and LAICI. NBO analyses were carried out using the CAM-B3LYP functional and the 6-31+G(d,p)basis set. In the case of the calculations using the 6-311++G(d,p) basis set, the corresponding NBOs could not be saved in the checkpoint files due to the large number of basis functions (1333 for LAIMe and 1307 for LAICI). Selected natural atomic orbital occupancies and NBO coefficients are listed in Supplementary Tables 20-23.

#### Data availability

The data that support the findings of this study are available in the Supplementary Materials of this article. All NMR spectra are provided as Supplementary Data 1–15. DFT-optimized geometries at  $S_0$  and  $S_1$  states of the compounds are provided as Supplementary Data 16. The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers 1880035 for LAICI, 1880036 for LAIMe, 2364980 for LAIBr, and 2364981 for LAII. These data can be obtained free of charge

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### **Author contributions**

S.I. performed the synthesis and characterization of all compounds, the photophysical measurements, and the theoretical calculations. T.H. performed the time-resolved PL measurements. K.T. and Y.C. supervised the research. All authors discussed the results and edited the manuscript.

### **Competing interests**

The authors declare no competing interests.

# Additional information

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