

Phosphorescence Property Modulation of β -Diketimate Aluminum Complexes by Utilizing Intraligand Charge Transfer States

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Keyword: Luminescence; Aluminum Complex; Diketimine

Abstract:

We report herein synthesis and optical properties of a series of aluminum hydride complexes with various β -diketiminate ligands having different electronic and steric features. From the measurements, dual emission properties consisting of fluorescence and phosphorescence were observed at 77 K. In particular, it was revealed that phosphorescence from the complexes was significantly affected by the substituent effect. The theoretical calculation data suggest that the electron-donating substituents should elevate the energy level of the T_2 state followed by the acceleration of the intersystem crossing of the S_1 – T_2 transition. These results mean that phosphorescence properties are able to be controlled by the substituent effect according to theoretical calculations without heavy atoms.

Introduction

β -Diketimate complexes of group 13 elements have been paid attention as a platform for constructing advanced luminescent materials.^[1–3] As a representative example, we have previously reported that boron β -diketimate complexes exhibit unique solid-state luminescence properties, such as aggregation- and crystallization-induced emission (AIE and CIE, respectively) properties as well as the dual emission properties involving fluorescence and phosphorescence at 77 K.^[4,5] Afterwards, we have also discovered phosphorescent materials based on β -diketimate complexes of different group 13 elements at 77 K.^[6–8] Furthermore, the introduction of either bromine or iodine onto the coordination center provided room-temperature phosphorescence property for the aluminum β -diketimate complexes.^[9] However, the detailed mechanism of their intersystem crossing (ISC) and the methodology to modulate the emission behaviors are still veiled.

Twisted donor–acceptor (TDA) structures, where donor and acceptor units are connected with a highly twisted conformation, have attracted great deal of attention because they often allow fast ISC followed by phosphorescence without heavy atoms.^[10,11] Since the total angular momentum must be conserved during electronic transitions, the change in an orbital angular momentum can allow ISC, where a spin angular momentum is changed because of the electron spin flipping. In the TDA systems, the electronic transition between a locally excited (LE) state within either the donor or acceptor units and a charge transfer (CT) state can induce the change in the orbital angular momentum, consequently facilitating fast ISC. The β -diketimate ligands possess twisted structures between the central N₂C₃ moiety and the peripheral aromatic rings, and it is known that the N₂C₃ moiety coordinated by group 13 elements is relatively

electron-deficient because of the electronegative nitrogen atoms and the element coordination.^[12] Therefore, the electronic transition from the electron-donating peripheral rings to the central N₂C₃ moiety should form an intraligand CT state. Indeed, some of β -diketiminato complexes with group 13 elements exhibit dual emission consisting of fluorescence and phosphorescence likely through the ISC from the singlet LE state to the triplet CT state.^[8,9] Interestingly, the intensity ratios between fluorescence and phosphorescence depend on the molecular structures.^[5] However, the structure–property relationships on their phosphorescence properties have been still unclear. To comprehend the photochemical mechanism, we hypothesized that the appropriate modifications of β -diketiminato complexes of group 13 elements might enable us to regulate emission via triplet states. In addition, we aimed to realize these photophysical processes with quantum chemical calculations.

In this study, considering β -diketiminato complexes as the TDA system, we examined electronic and luminescent properties of a series of aluminum hydride complexes with various β -diketiminato ligands having different electronic and steric features. From the optical measurements, it was found that the synthesized complexes can exhibit ligand-dependent dual emission including fluorescence and phosphorescence at 77 K. Moreover, phosphorescence intensity was influenced by the substituents. To explain photochemical properties, we discuss the dominant factors for the energy landscapes and the probability of ISC. This information could be applicable for designing phosphorescent materials without heavy atoms.

Results and Discussion

Synthesis

Aluminum dihydride complexes with β -diketiminate ligands were synthesized in two steps as shown in Figure 1a. First, the corresponding β -diketiminate ligands were obtained by the imine formation reactions of acetylacetone and the corresponding aniline derivatives. All aluminum hydride complexes except **MesLAIH** were prepared by the treatment of the ligands with 4 equivalent of lithium aluminum hydride in toluene. For the synthesis of **MesLAIH**, 1 equivalent of lithium aluminum hydride and diethyl ether were used. All compounds were fully characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and high-resolution mass spectrometry. In addition, the aluminum hydride complexes were also characterized by elemental analysis and single crystal X-ray diffraction (SCXRD) structure analysis (Figures 1b and S1). The large dihedral angles between the central AlN_2C_3 ring and substituted phenyl groups indicate their TDA-type structural feature: 92.40° and 89.89° for **DippLAIH**; 93.03° and 93.03° for **DMPLAIH**; 86.24° and 83.59° for **MesLAIH**; 95.01° and 85.65° for **MeOLAIH**. In addition, apparent π - π interaction was hardly observed in their crystal packing likely because of the sterically hindered substituents on the phenyl groups (Figure S1). Therefore, the photophysical properties might not significantly affected by intermolecular interactions. The detailed procedures and characterization data are shown in the Supporting Information.

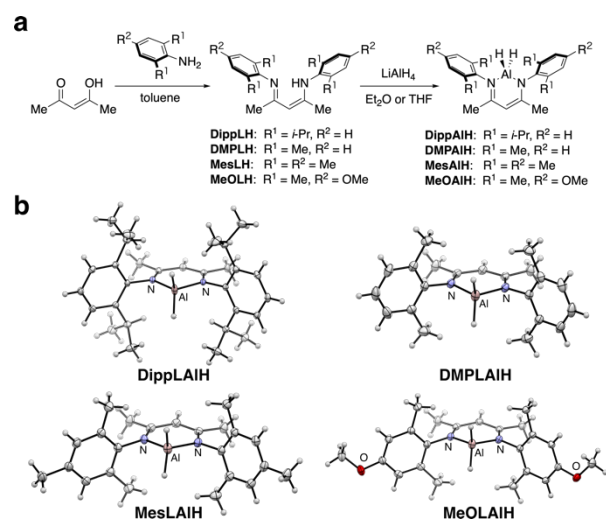


Figure 1. (a) Synthetic scheme of aluminum hydride complexes. (b) ORTEP of the complexes (ellipsoid: 50% of probability).

Photophysical properties at room temperature

All aluminum hydride complexes showed clear CIE property. The dilute solutions in 2-methylpentane (2MP; 1×10^{-5} M) showed almost no emission at the room temperature (Figure 2 and Table 1). It is because intramolecular motions and vibrations can accelerate decay of the excited state through non-radiative quenching processes. In contrast, the crystals of the complexes exhibited intense blue emission under UV irradiation (365 nm) at room temperature. Non-radiative decay processes should be suppressed because of restriction of molecular motions in the crystalline packing.

Their photophysical properties were investigated with UV-vis absorption and photoluminescence (PL) spectra at room temperature. The absorption spectra of all compounds in 2MP showed the large absorption bands in the UV region (339–346 nm). From the PL spectra with the 2MP solutions, weak broad emission bands were observed at around 380 nm from all compounds. In stark contrast to the solutions, their crystals significantly showed intense emission bands with the peaks at around 400–410 nm.

Moreover, the PL quantum yields (Φ_{PL}) of these crystals were dramatically enhanced (up to 0.51 for **DippLAIH**) than those of the solutions (< 0.01). Lifetime measurements in the crystalline states revealed that these emission bands both in solution and crystalline states were attributed to fluorescence because of their nanosecond-order lifetimes (Table S2).

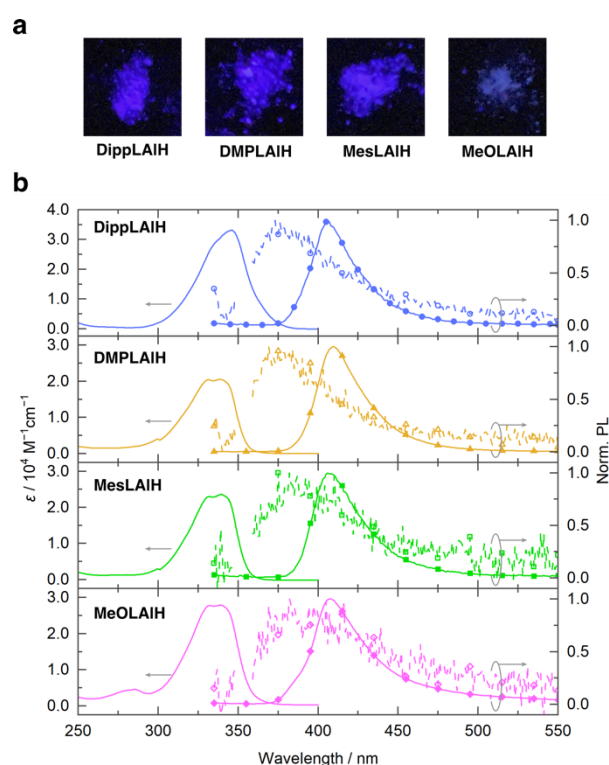


Figure 2. (a) Photographs of the crystals under UV irradiation (365 nm). (b) UV-vis absorption and PL spectra of solutions and crystals of aluminum complexes at room temperature. Legend: Solid line without symbols, absorption spectra; solid lines with filled symbols, PL spectra of crystals; dashed line with open symbols, PL spectra of solutions.

Table 1. Optical properties of aluminum hydride complexes at room temperature

	solution ^a				crystal ^d	
	λ_{abs} / nm	ϵ_{max} / $10^4 \text{ M}^{-1} \text{ cm}^{-1b}$	λ_{em} / nm ^c	Φ_{PL}^c	λ_{em} / nm ^c	Φ_{PL}^c
DippLAlH	346	3.3	378	<0.01	406	0.51
DMPLAlH	339	2.1	379	<0.01	409	0.31
MesLAlH	340	2.4	381	<0.01	406	0.39
MeOLAlH	339	2.8	382	<0.01	408	0.11

^a2-Methylpentane solution ($1 \times 10^{-5} \text{ M}$). ^bMolar absorption coefficients of the absorption maxima in the longest wavelength region. ^cExcited at λ_{abs} . ^dRecrystallized from toluene/hexane.

Photophysical Properties in solution at 77 K

To evaluate optical properties of single molecules without significant molecular motions as well as intermolecular interactions, we measured their PL, excitation and phosphorescence spectra in 2MP solutions at 77 K (Figure 3a). In clear contrast to the results at room temperature, they showed remarkably intense PL with two distinct emission bands in the regions of 370–394 and 436–440 nm (Table 2). Lifetime measurements under this condition revealed that the higher- and lower-energy emission bands should be attributed to fluorescence and phosphorescence according to the time ranges of lifetimes, respectively (Figure 3b,c, and Table S2). Such long-lifetime phosphorescence at 77 K (1.2–1.7 s) were also shown in the previous research on β -diketiminato complexes of group 13 elements.^[4,5] It is worth mentioning that their excitation spectra showed apparent vibrational structures. Furthermore, the PL quantum yield of the complexes reached over 0.80, especially 0.93 for **DippLAlH**, at 77 K. These observations indicate that the molecular motions, which cause non-radiative quenching of excited-state molecules, should be significantly restricted at 77 K.

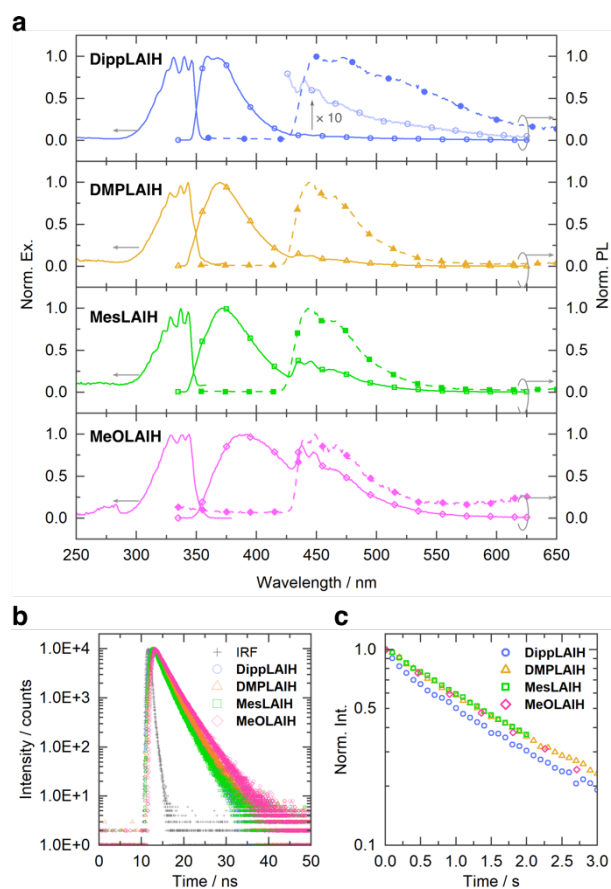


Figure 3. (a) Normalized PL (solid line, open symbols), excitation (solid line, without symbols), and phosphorescence (dashed line, filled symbols) spectra of the complexes in 2-methylpentane (1×10^{-5} M) at 77 K. Phosphorescence spectra were measured 10 ms after photoexcitation. PL decay curves measured at the PL maximum at around (b) 380 and (c) 450 nm. IRF denotes instrument response function.

It was worth noting that the phosphorescence intensity of **MeOLAIH** is largest among the complexes (Figure 3a and Table 2). The quantum yields of fluorescence and phosphorescence were estimated by calculating the integration ratio of each component. The phosphorescence quantum yields increased in the order of **DippLAIH**, **DMPLAIH**, **MesLAIH**, and **MeOLAIH**. These results indicate that phosphorescence intensities are controllable by the substituent effects.

Table 2. Optical properties of aluminum hydride complexes in 2-methylpentane (1×10^{-5} M) at 77 K

	$\lambda_{\text{em, FL}} / \text{nm}^a$	$\lambda_{\text{em, Phos}} / \text{nm}^a$	$\Phi_{\text{PL, all}}^a$	$\Phi_{\text{PL, FL}}^b$	$\Phi_{\text{PL, Phos}}^b$
DippLAIH	371	450	0.93	0.88	0.05
DMPLAIH	374	444	0.88	0.82	0.06
MesLAIH	376	443	0.86	0.70	0.15
MeOLAIH	392	449	0.81	0.63	0.17

^aExcited at λ_{abs} . ^bEstimated by calculating the integration ratios of fluorescence and phosphorescence in the steady-state spectrum.

Fluorescence, ISC, phosphorescence, and T_1-S_0 non-radiative decay rate constants (k_{FL} , k_{ISC} , k_{Phos} , and k_{nr}^T , respectively) were estimated from the results of quantum yields and lifetime measurements (Table 3). For this estimation, internal conversion from the lowest singlet excited state could be assumed to be much slower of the other decay processes (k_{FL} , $k_{\text{ISC}} \gg k_{\text{nr}}^S$) because molecular motions and intramolecular vibrational relaxations would be suppressed in frozen solution states at 77 K. In addition, reverse intersystem crossing (RISC) was also neglected because of the large energy gap (0.4–0.6 eV) between the lowest singlet and lowest triplet states. Importantly, it was revealed that **MesAIH** and **MeOLAIH**, which showed higher phosphorescence quantum yields (0.15–0.17) than the others (0.05–0.06) and possessed about twice k_{ISC} values ($1.3\text{--}1.4 \times 10^8 \text{ s}^{-1}$) of the others ($0.5\text{--}0.7 \times 10^8 \text{ s}^{-1}$).

Table 3. Photoluminescence rate constants of aluminum hydride complexes at 77 K

	$k_{\text{FL}} / 10^8 \text{ s}^{-1}^a$	$k_{\text{ISC}} / 10^8 \text{ s}^{-1}^b$	$k_{\text{Phos}} / \text{s}^{-1}^c$	$k_{\text{nr}}^T / \text{s}^{-1}^d$
DippLAIH	3.6	0.5	0.3	0.5
DMPLAIH	3.3	0.7	0.2	0.4
MesLAIH	3.2	1.4	0.3	0.3
MeOLAIH	2.3	1.3	0.3	0.3

$$^a k_{\text{FL}} = \Phi_{\text{FL}} / \langle \tau_{\text{FL}} \rangle, \quad ^b k_{\text{ISC}} = (1 - \Phi_{\text{FL}}) / \langle \tau_{\text{FL}} \rangle, \quad ^c k_{\text{Phos}} = \Phi_{\text{Phos}} / (1 - \Phi_{\text{FL}}) \tau_{\text{Phos}}, \quad ^d k_{\text{nr}}^{\text{T}} = (1 - \Phi_{\text{FL}} - \Phi_{\text{Phos}}) / (1 - \Phi_{\text{FL}}) \tau_{\text{Phos}}.$$

Theoretical Calculations

To obtain further insight into these differences in the photophysical properties, density functional theory (DFT), time-dependent DFT (TD-DFT) and TD-DFT calculations with the Tamm–Dancoff approximation performed with the Gaussian 16 revision C.01 package.^[13] the corresponding spin-orbit coupling constant between singlet and triplet states ($\zeta(S_m-T_n)$) were calculated with the Q-Chem 5.3 package.^[14] Geometry optimizations and single point energy calculations were carried out at the CAM-B3LYP/6-31+G(d,p) and the unrestricted M06/6-311++G(d,p) levels of theory, respectively (Figures S2 and S3 and Tables S4–S17). Geometry optimizations were performed in S_0 and S_1 states. Single-crystal structures and S_0 -optimized structures in the S_0 states were employed as initial geometries for the optimization at S_0 and S_1 states, respectively. All optimized structures were confirmed as local minima for each potential energy surface by using frequency calculations. The obtained S_0 and S_1 structures of each aluminum complex resemble that in the single crystal. Figure 4a shows the calculated energy diagrams in the S_1 states of the complexes. Importantly, energy gaps between S_1 and T_2 states decrease in the order of **DippLAlH**, **DMPLAlH**, **MesLAlH** and **MeOAlH**. This result shows good agreement with the order of k_{ISC} . In addition, the corresponding $\zeta(S_1-T_2)$ were calculated to be large enough to accept the ISC ($> 1 \text{ cm}^{-1}$, shown in Figure 4a as green text). Therefore, it is strongly suggested that the ISC of the aluminum complexes would occur mainly from S_1 to T_2 .

There might be two factors on efficient ISC progresses even without heavy atoms. First, the dimethyl-substituted complexes (**DMPLAIH**, **MesLAIH** and **MeOLAIH**) have more moderate twisted structures compared to diisopropyl-substituted one (**DippLAIH**). The change in the orbital angular momentum during the LE–CT ISC is maximized at 90° of dihedral angle between donor and acceptor moieties, whereas the orbital overlap between them diminishes with approaching such a perpendicular conformation. Consequently, it is implied that the dimethyl-substituted complexes might have more suitable dihedral angles for accelerating ISC than **DippLAIH**. Second, the electron-donating substituents on the aromatic ring could more effectively stabilize the T₂ state than the S₁ state, resulting in the narrower S₁–T₂ gap (Figure 4a). Natural transition orbital (NTO) analysis for S₁ and T₂ states of all complexes indicates that their S₁ states should be consisted of only LE transition, while their T₂ states are composed of both LE and CT transitions (Figure 4b, Table S12). Highest-occupied transition orbitals (HOTOs) and lowest-unoccupied transition orbitals (LUTOs) in the S₁ state of **MesLAIH** were mainly localized at the N2C3 component. This fact represents that the transition should have the LE character. On the other hand, the HOTO and LUTO in the T₂ state of **MesLAIH** distribute mainly at the aromatic rings on the nitrogen atoms and at the N2C3 moiety, respectively, suggesting that the transition should have the CT character. Additionally, in the T₂ state of **MesLAIH**, it is implied that the additional transition between HOTO–1 and LUTO+1 which localize at the aromatic groups might have the LE character. Importantly, the contribution ratio of the CT character in the T₂ states highly depends on the aromatic substituents. The stronger electron-donating substituent, *i.e.*, the methoxy group in **MeOLAIH**, can lead to the more significant contribution from the CT character, and indeed, the CT contribution reached 94 % for **MeOLAIH**.

Considering their Kohn–Sham frontier orbitals (Figure 4c,d), the HOTO and LUTO of the S_1 state of all compounds were attributable to the HOMO and LUMO, respectively. On the other hand, their CT-type HOTO and LUTO of the T_2 state were assignable to HOMO–1 and LUMO, respectively. Importantly, the HOMO–1 level is strongly destabilized by the electron-donating *para*-substituents in **MesLAIH** and **MeOLAIH**. On the other hand, the HOMO and LUMO levels are not significantly deviated by the substituents. This is because the substituents on the aromatic rings largely affect only to the HOMO–1 of the complexes. Consequently, the energy gap between HOMO–1 and LUMO should be efficiently narrowed by the methyl and methoxy groups, meanwhile the gap between HOMO and LUMO is only slightly altered. As a result, these electron-donating substituents made the S_1 – T_2 gap narrower, leading to the acceleration of ISC.

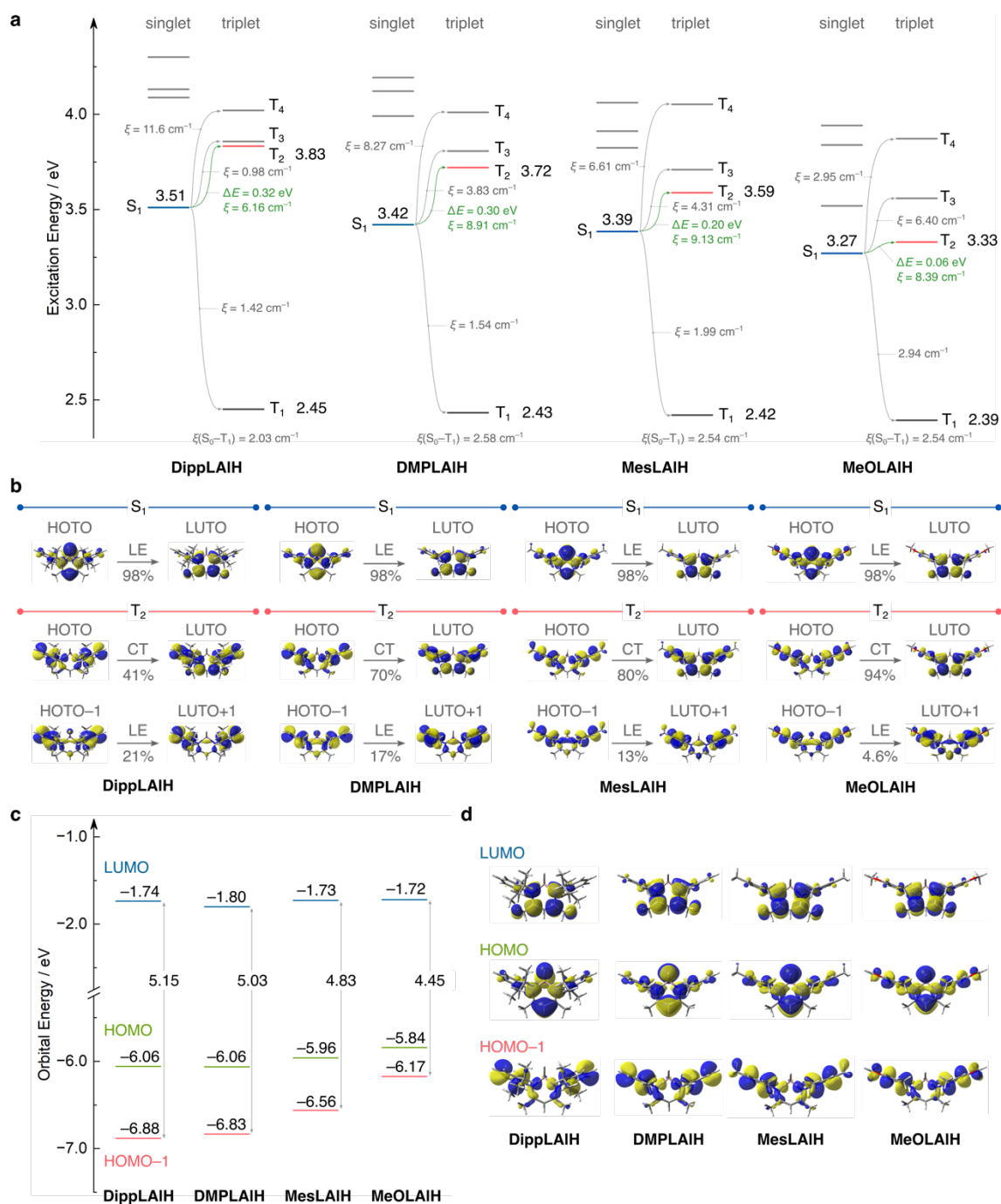


Figure 4. (a) Energy diagram of singlet and triplet excited states. Energy difference (ΔE) and SOC constant (ξ) for selected pairs of states are shown. (b) NTOs for S_1 and T_2 states (isovalue = 0.02). (c) Kohn–Sham frontier orbital energy diagram calculated with TD-DFT. (d) Kohn–Sham frontier orbital distributions (isovalue = 0.02).

Conclusion

We synthesized the new series of β -diketiminate dihydridoaluminum complexes and investigated their optical properties. It was demonstrated that the phosphorescence intensity of this class of complexes was able to be controlled by the electronic and steric features of the aromatic substituents on the nitrogen atoms. Importantly, the introduction of the electron-donating groups into these positions led to the destabilization of the molecular orbitals originating from these aromatic rings, resulting in the selective stabilization of the T_2 state relative to the S_1 state. Consequently, the S_1 – T_2 energy gap became narrower, and the ISC was accelerated. These results shed new light on the ways to control photophysical properties involving phosphorescence of not only β -diketiminate complexes but also the other typical element complexes, such as acetylacetonate and dipyrin complexes.

Crystallographic Data

Deposition Number(s) <url

href="https://www.ccdc.cam.ac.uk/services/structures?id=doi:

10.1002/ajoc.202500188">2422110 (for **MeOLAIH**), 2422111 (for **DippLAIH**),
2422112 (for **MesLAIH**), 2422113 (for **DMPLAIH**)</url> contain(s) the supplementary
crystallographic data for this paper. These data are provided free of charge by the joint
Cambridge

Crystallographic Data Centre and Fachinformationszentrum Karlsruhe <url

href="http://www.ccdc.cam.ac.

uk/structures">Access Structures service</url>.

Acknowledgments

Computation time was provided by the SuperComputer System, Institute for Chemical Research, Kyoto University. This work was partially supported by the Futaba Electronics Memorial Foundation and a Grant-in-Aid for Early-Career Scientists (for S.I., JSPS KAKENHI Grant Numbers 21K14673 and 23K13793) and for Scientific Research (B) (for K.T., JSPS KAKENHI Grant Number, 24K01570).

Conflict of Interest

The authors declare no conflict of interest.

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