Aluminium complexes of N_2O_2-type dipyrrins: the first hetero-multinuclear complexes of metallo-dipyrrins with high fluorescence quantum yields†

Chusaku Ikeda, Satoko Ueda and Tatsuya Nabeshima*

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The aluminium complexes of N_2O_2-dipyrrins were synthesized and the absorption/fluorescence spectral changes caused by the complex formation with $ZnCl_2$, $ZnBr_2$ and $Zn(OAc)_2$ were examined.

Boron dipyrrins such as BODIPY[1] (difluoroboradiaza-*s*-indacene) have been attracting considerable interest in many research areas due to their intense absorption and fluorescence in the visible region and their excellent photostability.[2] These complexes have found applications in biological labeling,[3] laser dyes,[4] paint or ink compositions, and electroluminescent devices.[5]

Since control of the fluorescence wavelength is important for practical applications, considerable efforts have been devoted to the modification of the BODIPY framework.[6–9] The synthesis of the fluorescent dipyrrin complexes with zinc(II),[9a] indium(III)[10] and gallium(III)[10] has also been reported, though their emission intensities are weaker than that of the BODIPY dye.

If fluorescent dipyrrin complexes have a coordination ability toward other metal ions, changes in the absorption/fluorescence wavelength upon subsequent complexation and fine-tuning of the optical properties by changing the metal ions or the counter ions are expected. Additionally, complexation between the dipyrrin metal complexes may afford multinuclear dipyrrin dimers. The formation of such molecular assemblies is fascinating as a novel method to afford supramolecular dipyrrin architectures.[11]

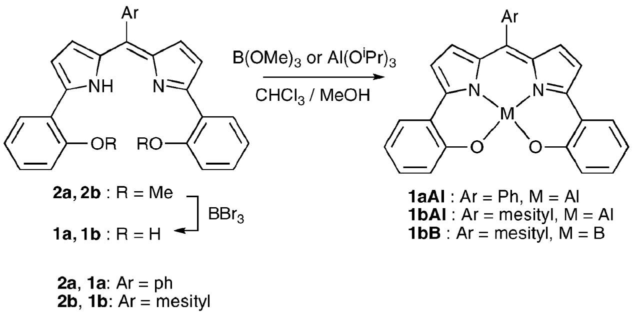
We have focused on studying the coordination ability of the dipyrrins bearing 2-hydroxyphenyl groups at the pyrrole-α positions (shown in Scheme 1) because complexation at the N_2O_2-type tetradentate binding site would afford a metalloligand as a bidentate ligand through its oxygen atoms. The combination of metals or counter anions may change the absorption/fluorescence wavelength of the metalloligands by unique coordination at the O_2-type chelate site.

To date, only a few complexes of N_2O_2-type dipyrrins have been reported. Bloom reported the nickel, cobalt and zinc complexes of an N_2O_2-type dipyrrin, though the emission properties of the complexes were not provided.[12] Recently, Burgess reported a boron complex of an N_2O_2-type dipyrrin that is highly fluorescent ($\Phi_F = 0.41$ in $CHCl_3$).[13] However, the chelating ability of the N_2O_2-type dipyrrin complexes has not hitherto been reported. We now chose aluminium as the central metal ion because (i) aluminium is ubiquitous and cheap and some aluminium complexes are highly fluorescent, (ii) the N_2O_2 binding site may serve as a planar equatorial unit for octahedral coordination geometry around aluminium, and (iii) oxygen atoms in the aluminium complexes are suitable for subsequent chelation because the oxygen atoms of the Al–O bonds are more negatively charged than those of the B–O bond.[14]

In this communication, we describe the synthesis and characterization of aluminium complexes of N_2O_2-type dipyrrins. The aluminium complexes further chelate to zinc(II) and an enhanced fluorescence was observed for the Al(III)–Zn(II) halide complexes. To the best of our knowledge, this is the first example of hetero-multinuclear complexes based on the dipyrrin framework.

The acid-catalyzed condensation of 2-(2-methoxyphenyl)-pyrrole and arylaldehyde in methylene chloride and subsequent oxidation with DDQ afforded the dipyrrin precursors **2a** and **2b** in 78 and 59% yield, respectively. Deprotections of the phenol moieties with BBr_3 quantitatively afforded the N_2O_2 dipyrrins **1a** and **1b**. Aluminium complexes **1aAl** and **1bAl** were quantitatively prepared from **1a** and **1b** by the reaction with $Al(O^iPr)_3$ in chloroform–methanol. The boron complex **1bB** was also prepared by treatment with $B(OMe)_3$.

Interestingly, the optical properties of the aluminium complexes drastically changed upon the addition of zinc(II) salts such as $ZnCl_2$ and $ZnBr_2$. Strong interactions between the aluminium complexes with the zinc(II) salts were supported by the absorption spectral changes. The addition of $ZnCl_2$ to **1aAl** in toluene–methanol (99 : 1) decreased the absorption at



Scheme 1

Gradate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki, 305-8577, Japan.
E-mail: nabesima@chem.tsukuba.ac.jp; Fax: +81-29-853-4507

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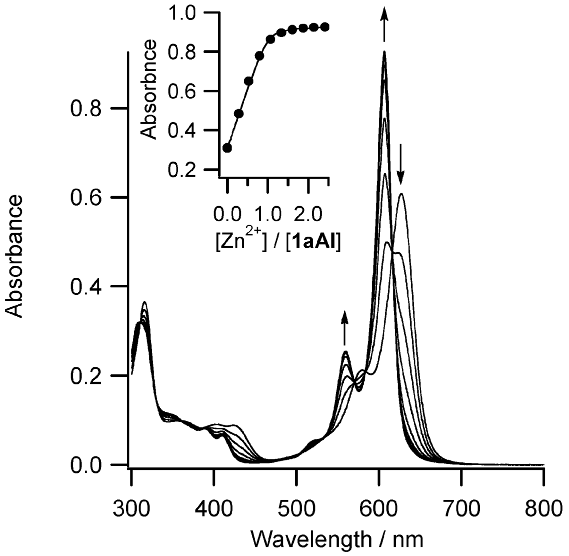

Fig. 1 Absorption spectral changes of **1aAl** upon addition of $ZnCl_2$. The inset shows the binding isotherm recorded at 607 nm with the calculated 1 : 1 binding curve (solid line): [**1aAl**] = 8.5 μM, 0 ≤ [Zn^{2+}]/[**1aAl**] ≤ 2.4, toluene–methanol (99 : 1).

627 nm with a concomitant increase in the absorption at 607 nm as shown in Fig. 1.

The 1 : 1 stoichiometry was suggested from the titration curve and the binding constant was evaluated to be $(6.1 \pm 1.1) \times 10^6\ M^{-1}$ from nonlinear least-squares regression analysis. Indeed, deep purple microcrystals of the 1 : 1 complex, **1aAl·ZnCl$_2$**, were obtained in 58% yield from a 1 : 1 mixture of **1aAl** and $ZnCl_2$. Similarly, the $ZnBr_2$ complex of **1aAl** and the $ZnCl_2$ complex of **1bAl** were obtained in 37 and 98% yields, respectively.

An X-ray crystallographic analysis revealed the structure of **1aAl·ZnCl$_2$** (Fig. 2).‡ The aluminium ion sits in the dipyrrin N_2O_2 site and has an octahedral coordination environment formed by the N_2O_2 donor atoms in the equatorial plane, and two water oxygen atoms in the axial position. The pyrrole rings and the phenol rings are nearly coplanar to afford the planar N_2O_2 site. The zinc(II) ion is coordinated with the two μ-phenoxo oxygen atoms (O1 and O2) and two chloride atoms. The tetrahedral structure of the zinc is slightly distorted with O–Zn–Cl, Cl–Zn–Cl and O–Zn–O bond angles of 112.0°,[15] 123.6° and 74.8°, respectively.

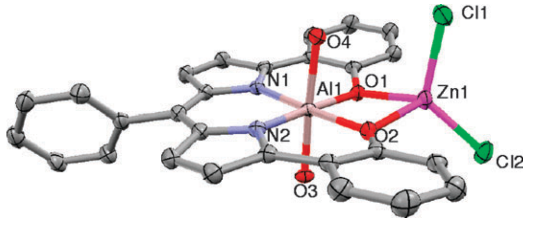

Fig. 2 Crystal structure of **1aAl·ZnCl$_2$**. Thermal ellipsoids are plotted at the 50% probability level. Hydrogen atoms and non-coordinating solvent molecules are omitted for clarity. Selected bond lengths (Å): Zn1–O1 2.0339(10), Zn1–O2 2.0296(10), Zn1–Cl1 2.2303(5), Zn1–Cl2 2.1815(4), Al1–O1 1.8720(10), Al1–O2 1.8701(10), Al1–N1 1.9363(12), Al1–N2 1.9364(12).

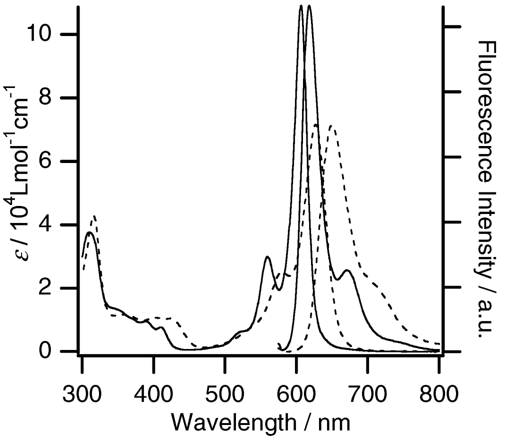

Fig. 3 Absorption and fluorescence spectra of **1aAl** (0.9 μM) in the absence (--) and presence (—) of excess $ZnCl_2$ in toluene–methanol (99 : 1). The samples were excited at 580 or 560 nm, respectively.

It is noteworthy that **1aAl·ZnCl$_2$** showed much sharper absorption and fluorescence spectral bands than **1aAl** (Fig. 3). The full widths at half-maximum height (fwhm) values of the absorption and fluorescence band of **1aAl** are 970 and 1120 cm^{-1}, but the corresponding values are 600 and 750 cm^{-1} in the presence of an excess amount of zinc(II) chloride. Additionally, the Stokes shift decreased from 560 to 360 cm^{-1} on zinc(II) complexation.

Also notable is the enhanced fluorescence of the zinc(II) complexes. The fluorescence quantum yield of **1aAl** increased from 0.23 to 0.55 upon binding to zinc(II) chloride (Table 1).

As shown in Table 1, **1aAl·ZnBr$_2$** also showed the same intense fluorescence as **1aAl·ZnCl$_2$**. The enhanced emission intensities of the Al(III)–Zn(II) halide complexes are probably due to the increased rigidity of the dipyrrin skeleton caused by the chelation, which reduced the loss of energy *via* radiationless thermal vibrations. As expected, **1bAl** and **1bAl·ZnCl$_2$** showed larger fluorescence quantum yields than **1aAl** and **1aAl·ZnCl$_2$**, respectively, probably due to the restricted rotation of the mesityl group.[9a] In contrast, the boron complex **1bB** showed no interaction with the zinc(II) salts. The distorted structure of the N_2O_2 binding site caused by the tetrahedral boron atom and lower negative charge of the oxygen atoms may suppress the coordination to the zinc(II) salts.[13]

On the other hand, the 2 : 1 complex, **(1aAl)$_2$·Zn(OAc)$_2$**, was obtained in 67% yield from a mixture of **1aAl** and zinc(II) acetate (instead of zinc(II) chloride). The fluorescence quantum yield of the 2 : 1 complex in solution was not determined due to dissociation under the dilute conditions (~1 μM).

Table 1 Optical properties of the N_2O_2-dipyrrin complexes

	λ_{abs}/nm	λ_{flu}/nm	Φ_F
1aAl	624	650	0.23
1bAl	625	647	0.72
1bB	626	645	0.72
1aAl·ZnCl$_2$[a]	607	620	0.55
1aAl·ZnBr$_2$[a]	607	620	0.56
1bAl·ZnCl$_2$[a]	608	619	0.83

[a] Recorded in the presence of an excess amount of zinc(II) salts to prevent dissociation.

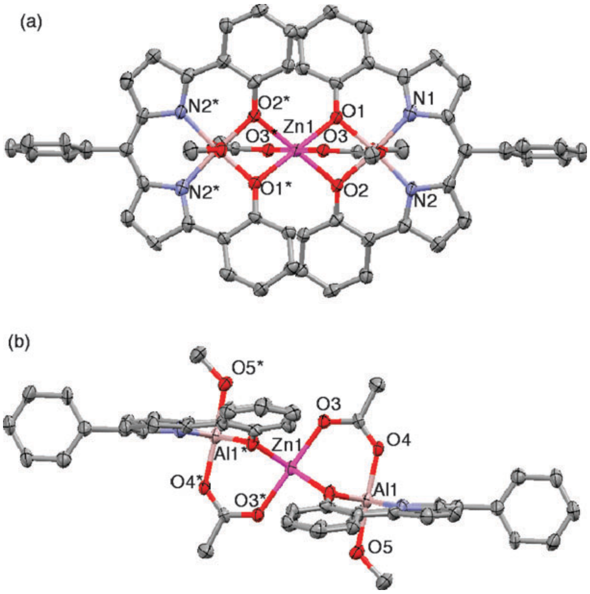

Fig. 4 Crystal structure of **(1aAl)$_2$·Zn(OAc)$_2$**. Thermal ellipsoids are plotted at 50% probability level: (a) and (b) show the top and side views, respectively. Hydrogen atoms and non-coordinating solvent molecules are omitted for clarity. One of the structures of **(1aAl)$_2$·Zn(OAc)$_2$** is shown for the two molecules in the asymmetric unit. Selected bond lengths (Å): Zn1–O1 2.071(4), Zn1–O2 2.143(4), Zn1–O3 2.112(4), Al1–O1 1.871(4), Al1–O2 1.860(5), Al1–O4 1.927(4), Al1–O5 1.964(4), Al1–N1 1.916(6), Al1–N2 1.933(5).

However, different optical properties of the 2 : 1 complex compared to that of the 1 : 1 complex were suggested from the absorption spectral pattern in which two strong absorption bands at 568 and 601 nm were observed (see Fig. S1†). X-Ray crystallographic study revealed that the two **1aAl** moieties are bridged by a zinc(II) ion (Fig. 4).‡ The trinuclear dimeric structure is stabilized by the two μ-acetate ligands bridging Al1–Zn1 and Al1*–Zn1. The μ-phenoxo oxygen atoms (O1 and O2) of the dipyrrin coordinate to Zn1 at the inversion center to give octahedral geometry. Since the dimeric complex is labile, the complexation of analogues of the aluminium complex with Zn(OAc)$_2$ could be applied to the construction of dynamic dipyrrin assemblies.

In conclusion, novel aluminium complexes of an N$_2$O$_2$-type dipyrrin were synthesized and their complexes with ZnCl$_2$, ZnBr$_2$ and Zn(OAc)$_2$ were characterized. The fluorescence wavelength and the intensity of the aluminium complexes drastically changed upon Zn complex formation. The results obtained in this study can be applied not only to tunable fluorescence materials, but also to metallosupramolecules with cation-responding properties. We are currently studying other multinuclear complexes based on N$_2$O$_2$-type dipyrrins which possess interesting optical and magnetic properties.

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Notes and references

‡ *Crystal data* for [**1a**Al·ZnCl$_2$(H$_2$O)$_2$]·3Et$_2$O: C$_{39}$H$_{51}$AlCl$_2$N$_2$O$_7$Zn, M = 823.07, monoclinic, space group $P2_1/n$ (no. 14), a = 10.7486(3), b = 24.8464(7), c = 15.2711(4) Å, β = 98.9556(11)°, U = 4028.64(19) Å^3, T = 120 K, Z = 4, 37 895 reflections measured, 9161 unique (R_{int} = 0.0258). $R1$ = 0.0307 ($I > 2\sigma(I)$), $wR2$ = 0.0881 (all data), GOF(F^2) = 1.066.[16]

Crystal data for [(**1b**Al)$_2$·Zn(OAc)$_2$(MeOH)$_2$]·MeOH: C$_{126}$H$_{110}$Al$_4$Cl$_6$-N$_8$O$_{24}$Zn$_2$, M = 2571.58, triclinic, space group $P\bar{1}$ (no. 2), a = 11.2352(7), b = 14.0083(10), c = 19.4195(13) Å, α = 70.594(2), β = 89.998(2), γ = 87.1542(18)°, U = 2878.7(3) Å^3, T = 120 K, Z = 2, 28 385 reflections measured, 12999 unique (R_{int} = 0.1202). $R1$ = 0.0777 ($I > 2\sigma(I)$), w$R2$ = 0.2200 (all data), GOF(F^2) = 1.057.[16]

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