Supplementary information

Aluminum complex of N$_2$O$_2$-type dipyrrin: the first hetero-multinuclear complexes of metallo-dipyrrin with high fluorescence quantum yields

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1. General

All chemicals were reagent grade, and used without further purification. THF was purified by distillation from benzophenone ketyl under argon atmosphere before use. All reactions were performed under nitrogen atmosphere. 

$N$-tert-butoxycarbonyl-2-bromopyrrole was prepared as previously described. Column chromatography was performed with Kanto Chemical silica gel 60 N (spherical, neutral) or Wako Chemical alumina (activated, about 200 mesh). $^1$H NMR spectra were recorded on a Bruker ARX400 spectrometer at 400 MHz, or a Bruker AC300 spectrometer at 300 MHz. $^{13}$C NMR spectra were recorded on a Bruker ARX400
spectrometer at 100 MHz. In both NMR measurements, tetramethylsilane was used as an internal standard. UV-Vis spectra were recorded on JASCO V-660 spectrophotometer. Fluorescence spectra and absolute quantum yields were measured on a Hitachi F-4500 spectrometer and a Hamamatsu Photonics absolute PL quantum yield measurement system C9920-02, respectively. Mass spectra (ESI-TOF, positive mode) were recorded on an Applied Biosystems QStar Pulsar i spectrometer. Elemental analyses were performed at Chemical Analysis Center, University of Tsukuba.

2. Synthesis

Synthetic scheme

\[ \text{Dipyrrin 2a} \]

To a stirred solution containing 2-(2-methoxyphenyl)pyrrole (0.82 g, 4.7 mmol) and benzaldehyde (0.25 mL, 2.4 mmol) in CH\(_2\)Cl\(_2\) (100 mL) was added trifluoroacetic acid (TFA) (55 µL, 0.71 mmol) under nitrogen atmosphere and the mixture was stirred for 2 h. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.54 g, 2.4 mmol) was added and the resulting solution was stirred further 1.5 h. The reaction mixture was washed with saturated NaHCO\(_3\) aqueous solution, dried over Na\(_2\)SO\(_4\), and evaporated to small
volume that was loaded directly on the short alumina column and eluted with CH$_2$Cl$_2$. The first red band was collected and purified again using short SiO$_2$ column eluted with CH$_2$Cl$_2$ to CH$_2$Cl$_2$–ethyl acetate (5:2). Red fraction was collected, evaporated to dryness, and recrystallized from Et$_2$O/hexane to give 2a (0.80 g, 78%). $^1$H NMR (300 MHz, CDCl$_3$) δ 3.84 (s, 6H), 6.62 (d, 2H, $J = 4.3$ Hz), 6.93 (d, 2H, $J = 4.3$ Hz), 6.97-7.05 (m, 4H), 6.97-7.05 (m, 4H), 7.31 (td, 2H, $J = 7.7$ and 1.6 Hz), 7.43-7.45 (m, 3H), 7.53-7.56 (m, 2H), 7.68 (dd, 2H, $J = 7.7$ Hz and 1.6 Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 55.95, 111.60, 118.34, 120.92, 122.57, 127.50, 128.46, 128.59, 129.07, 129.68, 130.99, 137.95, 139.26, 141.05, 152.26, 157.34. ESI-MS observed $m/z$ 433.2 ([M+H]$^+$). Anal. Calcd for C$_{29}$H$_{24}$N$_2$O$_2$ • 0.15H$_2$O: C, 80.03; H, 5.63; N, 6.44. Found C, 80.12; H, 5.82; N, 6.33. 

**Dipyrrin 2b**

To a stirred solution containing 2-(2-methoxyphenyl)pyrrole (0.52 g, 3.0 mmol) and mesitaldehyde (0.22 mL, 1.5 mmol) in CH$_2$Cl$_2$ (90 mL) was added TFA (35 µL, 0.45 mmol) under nitrogen atmosphere and the mixture was stirred for 4 h. DDQ (0.34 g, 1.5 mmol) was added and the resulting solution was stirred further 8 h. The reaction mixture was washed with saturated NaHCO$_3$ aqueous solution, dried over Na$_2$SO$_4$, and evaporated to small volume that was loaded directly on the short alumina column and eluted with CH$_2$Cl$_2$. The first red band was collected and purified again using short SiO$_2$ column eluted with hexane–ethyl acetate (10:1 to 10:3). Red fraction was collected, evaporated to dryness, and recrystallized from CH$_2$Cl$_2$/MeOH to give 2b (0.42 g, 59%). $^1$H NMR (400 MHz, CDCl$_3$) δ 2.17 (s, 6H), 2.36 (s, 3H), 3.90 (s, 6H), 6.40 (d, 2H, $J = 4.2$ Hz), 6.87 (d, 2H, $J = 4.2$ Hz), 6.93 (s, 2H), 6.99-7.06 (m, 4H), 7.31 (td, 2H, $J = 7.7$ Hz and 1.6 Hz), 8.07 (dd, $J = 7.7$ Hz and 1.6 Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 20.18, 21.13, 55.9, 111.57, 118.33, 120.86, 122.59, 127.08, 127.67,
129.02, 129.54, 134.11, 137.10, 137.93, 140.81, 151.91, 157.30. ESI-MS observed m/z 475.5 ([M+H]+). Anal. Cald for C$_{32}$H$_{30}$N$_{2}$O$_{2}$: C, 80.97; H, 6.37; N, 5.90. Found C, 80.73; H, 6.50; N, 5.75.

**Dipyrrin 1a**

To a stirred solution containing 2a (0.80 g, 1.85 mmol) in CH$_2$Cl$_2$ (30 mL) was added BBr$_3$ (1. 7 mL, 18 mmol) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred overnight allowing to warm up to room temperature and quenched with methanol (ca. 50 mL). The mixture was evaporated and dissolved again with methanol (100 mL). To the obtained mixture was added conc. HCl (ca. 5 mL) and refluxed for 3 hrs. After cooled down, the mixture was neutralized with saturated NaHCO$_3$ aqueous solution and extracted with ethyl acetate. The organic layer was dried over Na$_2$SO$_4$, evaporated to dryness, and recrystallized from THF/hexane to give 1a (0.72 g, 96%). $^1$H NMR (CDCl$_3$, 400 MHz) δ 6.70 (d, 2H, $J = 4.3$ Hz), 6.88 (t, 2H, $J = 7.4$ Hz), 6.93-6.97 (m, 4H), 7.09 (td, 2H, $J = 7.7$ Hz and 1.5 Hz), 7.46-7.56 (m, 5H), 7.66 (dd, 2H, $J = 7.8$ Hz and 1.5 Hz). $^{13}$C NMR (DMSO-$d_6$, 100 MHz) δ 116.7, 117.3, 119.5, 127.8, 127.9, 129.2, 129.4, 130.2, 131.2, 137.4, 138.7, 139.2, 153.6, 156.4. ESI-MS observed m/z 405.2 ([M+H]+). Anal. Cald for C$_{27}$H$_{20}$N$_{2}$O$_{2}$•0.5THF: C, 79.07; H, 5.49; N, 6.36. Found C,79.40; H, 5.42; N, 6.12.

**Dipyrrin 1b**

1b was synthesized following the procedure for 1a. Reaction of 2b (340 mg, 0.72 mmol) and BBr$_3$ (1.5 mL, 1.4 mmol) followed by same workup procedure afforded 2b (314 mg, 97%). $^1$H NMR (CDCl$_3$, 400 MHz) δ 2.16(s, 6H), 2.38(s, 3H), 6.51(d, 2H, $J$
= 3.8 Hz), 6.84-6.89 (m, 4H), 6.96-6.98 (m, 4H), 7.05 (t, 2H, J = 7.0 Hz), 7.63 (dd, 2H, J = 7.8 Hz and 1.4 Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.0, 21.1, 115.4, 116.9, 117.8, 120.1, 127.8, 127.9, 128.9, 130.0, 134.5, 137.1, 137.6, 138.7, 153.9, 156.0. ESI-MS observed m/z 447.2 ([M+H]$^+$). Anal. Cald for C$_{30}$H$_{26}$N$_2$O$_2$•0.25H$_2$O: C, 79.89; H, 5.92; N, 6.21. Found C, 80.18, H, 6.08; N, 6.03.

1aAl

To a stirred solution containing 1a (63.0 mg, 0.16 mmol) in 10 mL of CHCl$_3$–MeOH (1:1) was added Al(OiPr)$_3$ (63.7 mg, 0.30 mmol) and the reaction mixture was refluxed for 4 h. After being cooled, the mixture was evaporated to dryness and the residue was purified by column chromatography on silica gel using hexane-ethyl acetate (1:1) as eluent, and recrystallized from CH$_2$Cl$_2$/CH$_3$OH to give 1aAl (65.7 mg, 98%). $^1$H NMR (CDCl$_3$-CD$_3$OD (1:1), 400 MHz) $\delta$ 6.51 (d, J = 4.4 Hz, 2H), 6.61 (t, J = 7.0 Hz, 2H), 6.80 (d, J = 4.4 Hz), 6.91 (d, J = 8.0 Hz, 2H), 7.11 (t, J = 8.0 Hz, 2H), 7.43-7.48 (m, 5H), 7.54 (d, J = 7.0 Hz, 2H). $^{13}$C NMR (DMSO-$d_6$, 100 MHz) $\delta$ 114.4, 114.6, 127.2, 127.4, 128.0, 129.3, 129.9, 130.0, 138.3, 139.2, 139.4, 157.1, 162.6. ESI-MS observed m/z 429.1 ([M+H]$^+$). Anal. Cald for C$_{27}$H$_{17}$AlN$_2$O$_2$•0.75CH$_3$OH: C, 73.67; H, 4.46; N, 6.19. Found C, 73.66; H, 4.65; N, 6.04.

1bAl

1bAl was quantitatively synthesized following the procedure described for 1aAl. $^1$H NMR (CDCl$_3$-CD$_3$OD (1:1), 400 MHz) $\delta$ 2.15 (s, 6H), 2.36 (s, 3H), 6.36 (d, J = 4.3 Hz, 2H), 6.59 (td, J = 7.4 and 1.0 Hz, 2H), 6.74 (d, J = 4.3 Hz, 2H), 6.88 (dd, J = 8.3 and 1.0 Hz, 2H), 6.94 (s, 2H), 7.07 (t, J = 6.9 Hz, 2H), 7.52 (dd, J = 7.8 and 1.6 Hz,
$^1$H NMR (CDCl$_3$-CD$_3$OD 1:1, 400 MHz) $\delta$ 2.13 (s, 6H), 2.39 (s, 3H), 6.86 (m, 2H), 6.91 (m, 2H), 6.95 (d, $J = 8.3$ Hz, 2H), 7.01 (s, 2H), 7.10 (m, 2H), 7.37 (t, $J = 7.8$ Hz, 2H), 7.83 (d, $J = 7.9$ Hz, 2H). ESI-MS observed $m/z$ 455.3 ([M+H]$^+$). Anal. Cald for C$_{30}$H$_{23}$N$_2$O$_2$·MeOH: C, 76.55; H, 5.60; N, 5.76. Found C, 76.66; H, 5.53; N, 5.76.

**General procedure for the zinc complexes**

To a solution containing 1a or 1b (10 mg, 2 × 10$^{-5}$ mmol) in CHCl$_3$ (5 mL), 1 equivalent of zinc(II) halide or 0.5 equivalent of zinc(II) acetate in MeOH (1 mL) was added. After stirred for 10 min, the solvent was evaporated and the residue was recrystallized to give zinc-aluminum complexes.

1aAl•ZnCl$_2$

Recrystallized from Et$_2$O/hexane. Yield was 58%. $^1$H NMR (CDCl$_3$-CD$_3$OD
(99:1), 400 MHz) δ 6.68 (d, J = 4.4 Hz, 2H), 6.91 (t, J = 6.8 Hz, 2H), 6.93 (d, J = 4.4 Hz, 2H), 7.24-7.32 (m, 4H), 7.47-7.51 (m, 5H), 7.68 (d, J = 7.6 Hz). 13C NMR (CDCl3-CD3OD (99:1), 100 MHz) δ 115.9, 119.2, 120.4, 120.5, 127.7, 128.4, 128.9, 130.5, 131.7, 132.4, 137.4, 140.1, 142.8, 155.5, 156.6. Anal. Cald for C27H17AlCl2N2O2Zn•3.5H2O•Et2O: C, 53.05; H, 4.88; N, 3.99. Found C, 52.98; H, 4.68; N, 3.85.

1aAl•ZnBr2

Recrystallized from CH2Cl2/hexane. Yield was 37%. 1H NMR (CDCl3-CD3OD (99:1), 400 MHz) δ 6.69 (d, J = 4.4 Hz, 2H), 6.91 (td, J = 7.6 and 1.0 Hz, 2H), 6.93 (d, J = 4.4 Hz, 2H), 7.26 (m, 2H), 7.40 (dd, J = 8.0 and 1.0 Hz, 2H), 7.47-7.52 (m, 5H), 7.69 (dd, J = 8.0 and 1.6 Hz). 13C NMR (CDCl3-CD3OD (99:1), 100 MHz) δ 115.8, 119.3, 120.4, 120.7, 127.6, 128.4, 128.9, 130.5, 131.6, 132.4, 137.5, 140.1, 142.8, 155.6, 156.5. Anal. Cald for C27H17AlBr2N2O2Zn•0.25C6H14: C, 50.70; H, 3.06; N, 4.15. Found C, 51.10; H, 3.15; N, 4.16.

1bAl•ZnCl2

Recrystallized from CH2Cl2/CH3OH. Yield was 98%. 1H NMR (CDCl3-CD3OD (99:1), 400 MHz) δ 2.14 (s, 6H), 2.39 (s, 3H), 6.55 (d, J = 4.4 Hz, 2H), 6.88 (d, J = 4.4 Hz, 2H), 6.91 (td, J = 6.8 and 1.4 Hz, 2H), 6.98 (s, 2H), 7.24-7.32 (m, 2H), 7.67 (dd, J = 8.0 and 1.6 Hz). 13C NMR (CDCl3-CD3OD (99:1), 100 MHz) δ 19.7, 21.1, 115.8, 119.3, 120.3, 120.5, 128.0, 128.3, 130.7, 131.5, 133.7, 136.4, 137.8, 139.7, 142.1, 155.5, 156.2. Anal. Cald for C30H23AlCl2N2O2Zn•4CH3OH•1H2O: C, 54.23; H, 5.49; N, 3.72. Found: C, 54.41; H, 5.37; N 3.62.
(1aAl)_2*Zn(OAc)_2

Recrystallized from CHCl_3/CH_3OH. Yield was 67%. ^1H NMR (CDCl_3-CD_3OD (99:1), 400 MHz) δ 2.05 (s, 3H), 6.51-6.57 (m, 4H), 6.64 (d, J = 4.4 Hz, 2H), 6.66-6.69 (m, 2H), 6.80 (d, J = 4.4 Hz), 7.46-7.48 (m, 6H), 7.65 (br. 1H). ^13C NMR (CDCl_3-CD_3OD (99:1), 100 MHz) δ 24.0, 114.8, 118.4, 120.4, 121.6, 127.5, 128.3, 129.7, 130.5, 130.7, 138.3, 140.2, 140.4, 142.3, 156.5, 157.3, 178.2. Anal. Cald for C_{58}H_{40}Al_2N_4O_8Zn*2H_2O: C, 64.72; H, 4.12; N, 5.21. Found C, 64.88; H, 4.20; N, 5.09.
3. UV-vis spectra of \((1\text{aAl})_2\cdot\text{Zn(OAc)}_2\)

![UV-vis spectra of \((1\text{aAl})_2\cdot\text{Zn(OAc)}_2\).](image.png)

**Fig. S1.** Absorption spectra of \((1\text{aAl})_2\cdot\text{Zn(OAc)}_2\). \([1\text{aAl}] = 80 \mu\text{M, toluene–methanol (99:1). Optical path length = 1.0 mm.}

**Reference**