*The Supporting Information for*

# Synthesis of a New Family of Ionophores Based on Aluminum-Dipyrrin Complexes (ALDIPYs) and Their Strong Recognition of Alkaline Earth Ions

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**Contents**

**Materials and Methods**

**Synthesis and characterization of the compounds**

**X-ray crystallographic analysis**

**Recognition of alkaline earth ions**

**References for the Supporting Information**

## Materials and Methods

Unless otherwise noted, solvents and reagents were purchased from TCI Co., Ltd., Wako Pure Chemical Industries, Ltd., Kanto Chemical Co., Inc., Nacalai Tesque, Inc. or Sigma-Aldrich Co., and used without further purification. Silica gel for column chromatography was purchased from Kanto Chemical Co. Inc. (Silica Gel 60 N (spherical, neutral, 63–210 μm). Alumina for column chromatography was purchased from Wako Pure Chemical Industries, Ltd. (alumina, activated (about 75 μm)). GPC purification was performed on a JAI LC-9210 II NEXT system with JAIGEL-1HH/2HH columns using $CHCl_3$ as an eluent.

$^1H$, $^{13}C$, NMR, and other 2D NMR spectra were recorded on a Bruker AVANCE III-400, 500, or 600 spectrometers. Negative values were depicted in red in the spectra. Tetramethylsilane was used as an internal standard (δ 0.00 ppm) for $^1H$ and $^{13}C$ NMR measurements when $CDCl_3$ was used as a solvent.

Single-crystal X-ray crystallographic measurements were performed using a Bruker APEX II ULTRA with Mo$K\alpha$ radiation. Obtained data were processed using a Bruker APEX2[S2] and Yadokari-XG[S3] crystallographic software package except for refinement, which was performed using SHELXL-2014[S4]. CCDC 1446110 ([**1**·($CH_3OH$)($H_2O$)]), 1446111 (**3**), 1446112 ([**2**·$(CH_3OH)_4$]), 1446113 (**13**) and 1446114 (**6**) contain the data for the structures. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

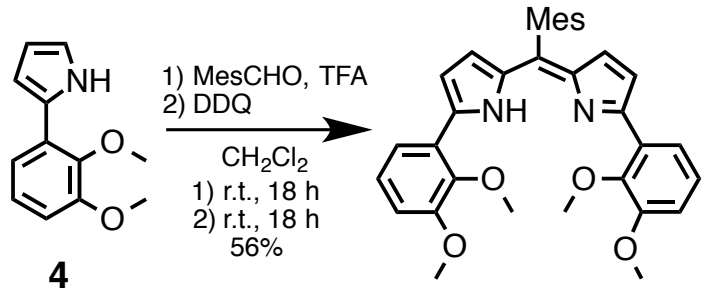
MALDI-TOF mass data were recorded on an AB SCIEX TOF/TOF 5800 system. ESI-TOF mass data were recorded on an AB SCIEX TripleTOF 4600 system.

UV-Vis spectra were recorded on a JASCO V-670 spectrophotometer. Emission spectra were recorded on a JASCO FP-8600 fluorescence spectrophotometer. Absolute fluorescence quantum yields were determined with a Hamamatsu Photonics absolute PL quantum yield measurement system C9920-02. Solvents used for measurements were air-saturated.

Elemental analysis was performed on a Yanaco MT-6 analyzer with tin boats purchased from Elementar. We appreciate Mr. Ikuo Iida for the measurements.

**Synthesis and characterization of the compounds**

**Scheme S1.** Synthesis of **5**




**4** **5**

A round-bottom flask was charged with **4**[S5] (1.53 g, 7.53 mmol) and dichloromethane (60 mL). The solution was deoxygenated by vacuum–$N_2$ cycles. 2,4,6-trimethylbenzaldehyde (0.546 mL, 3.77 mmol) was added to the flask. Trifluoroacetic acid (0.175 mL, 2.27 mmol) was added and the mixture was stirred under nitrogen at room temperature in the dark for 18 h. DDQ (0.856 g, 3.77 mmol) was added and the mixture was stirred under nitrogen at room temperature in the dark for another 18 h. Triethylamine (1 mL, 7 mmol) was added and the reaction mixture was loaded onto a short alumina-gel column and eluted with dichloromethane, followed by ethyl acetate. Eluted bands were collected and concentrated in vacuo, which was purified by column chromatography on silica gel (eluent: $CH_2Cl_2$ : AcOEt = 100 : 0 ~ 0 : 100) to give **5** (1.13 g, 2.12 mmol, 56%).

**5**: red crystal;

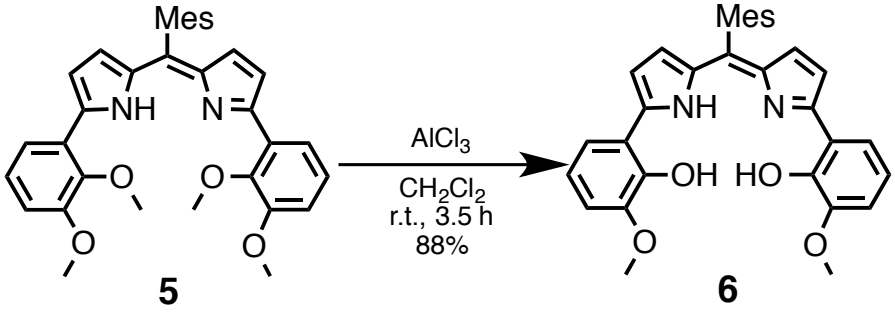
m.p. 86–88 °C.

$^1$H NMR (400 MHz, $CDCl_3$) δ 13.66 (br, 1H), 7.80 (d, *J* = 7.5 Hz, 2H), 7.15 (dd, *J* = 8.0, 7.5 Hz, 2H), 6.94–6.92 (m, 6H), 6.42 (d, *J* = 4.2 Hz, 2H), 3.93 (s, 6H), 3.88 (s, 6H), 2.37 (s, 3H), 2.17 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 153.5, 151.6, 147.7, 141.1, 138.1, 137.2, 137.0, 133.9, 127.71, 127.52, 127.1, 124.1, 120.8, 118.6, 112.8, 60.8, 56.2, 21.1, 20.1.

Elemental analysis: Calcd for $C_{34}H_{34}N_2O_4$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.17; H, 6.51; N, 5.01.

**Scheme S2.** Synthesis of **6**




A round-bottom flask was charged with **5** (1.13 g, 2.12 mmol). Dichloromethane (150 mL) and aluminum trichloride (14.1 g, 150 mmol) was added to the flask. The mixture was stirred at room temperature for 1 h. 1 M HCl (100 mL) was added on an ice bath, and subsequently sat. $NaHCO_3$aq (100 mL) was added. The mixture was separated, and the aqueous layer was extracted with ethyl acetate (40 mL × 3). The combined organic layer was dried over $Na_2SO_4$, filtered, and concentrated in vacuo to give **6** (0.941 g, 1.86 mmol, 88%)

**6**: purple crystal;

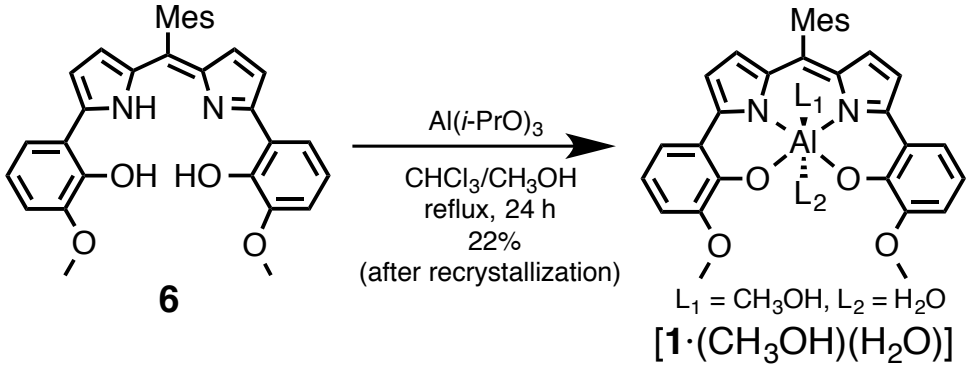
m.p. 232–233 °C.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.28–7.26 (m, 3H), 6.95 (s, 2H), 6.86–6.77 (m, 6H), 6.51 (br, 2H), 3.87 (s, 6H), 2.38 (s, 3H), 2.13 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 146.2, 137.5, 137.1, 127.9, 119.6, 119.2, 111.4, 56.0, 21.2, 20.0. Some signals were severely broadened and not observed clearly probably due to chemical exchange at a rate similar to the NMR time scale.

Elemental analysis: Calcd for $C_{32}H_{30}N_2O_4$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.66; H, 6.08; N, 5.35.

**Scheme S3.** Synthesis of ALDIPY monomer [**1**·($CH_3OH$)($H_2O$)]




A 10 mL round-bottom flask was charged with **6** (78.3 mg, 0.155 mmol) and aluminum triisopropoxide (63.6 mg, 0.311 mmol). Chloroform (4 mL) and methanol (4 mL) was added to the flask. The mixture was refluxed for 13 h. After cooling, the solution was concentrated in vacuo. The crude was purified by column chromatography on alumina gel (eluent: $CHCl_3$ : methanol = 100 : 0 ~ 0 : 100). Reprecipitation from dichloromethane / methanol gave [**1**·($CH_3OH$)($H_2O$)] (19.9 mg, 0.0343 mmol, 22%).

[**1**·($CH_3OH$)($H_2O$)]: dark green crystal;

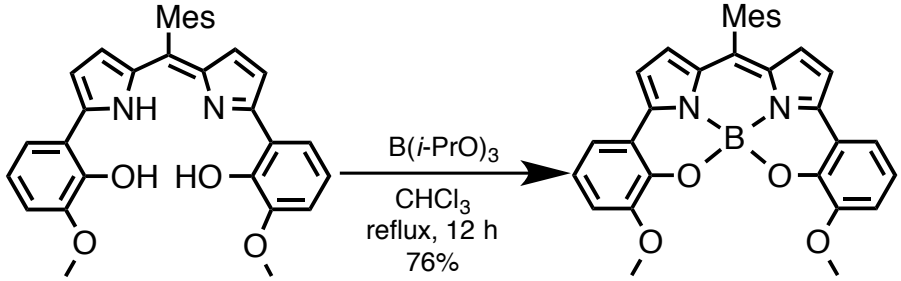
m.p. >280 °C.

$^1$H NMR (400 MHz, $CDCl_3$/$CD_3OD$ = 1:1 (v/v)) δ 7.24 (d, $J$ = 7.4 Hz, 2H), 6.96 (s, 2H), 6.80 (t, $J$ = 5.8 Hz, 4H), 6.62 (t, $J$ = 7.9 Hz, 2H), 6.42 (d, $J$ = 4.3 Hz, 2H), 3.94 (s, 6H), 2.38 (s, 3H), 2.17 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 158.3, 151.5, 151.0, 141.0, 140.5, 137.9, 137.2, 135.3, 130.1, 128.3, 120.5, 120.3, 116.3, 115.7, 111.0, 55.6, 21.2, 19.9.

Elemental analysis: Calcd for $C_{33}H_{33.4}AlN_2O_{6.2}$ ([**1**·1.2($H_2O$)($CH_3OH$)]: C, 67.84; H, 5.76; N, 4.80. Found: C, 67.71; H, 5.47; N, 4.95.

**Scheme S4.** Synthesis of **3**




**6** **3**

A 100 mL round-bottom flask was charged with **6** (99.5 mg, 0.196 mmol). Chloroform (50 mL) and triisopropyl borate (0.450 mL, 1.96 mmol) was added to the flask. The mixture was refluxed for 12 h. After cooling, water (30 mL) was added, and the mixture was extracted with chloroform (10 mL × 2). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude was purified by column chromatography on silica gel using dichloromethane as the eluent. Reprecipitation from dichloromethane / *n*-hexane gave **3** (76.5 mg, 0.149 mmol, 76%).

**3**: dark red crystal;

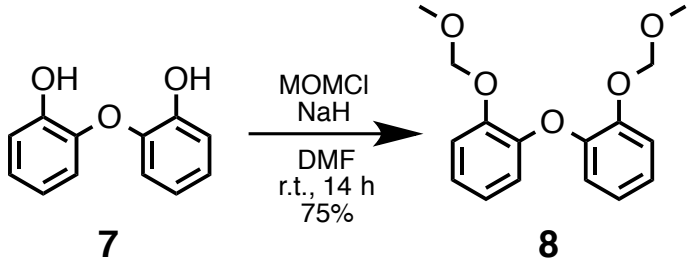
m.p. > 280 °C.

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2H), 6.97–6.95 (m, 6H), 6.80 (d, $J$ = 4.3 Hz, 2H), 6.79 (d, $J$ = 4.3 Hz, 2H), 3.65 (s, 6H), 2.36 (s, 3H), 2.09 (s, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 150.9, 150.4, 144.7, 138.5, 137.8, 137.1, 134.9, 129.4, 128.2, 127.9, 120.4, 120.0, 118.7, 116.4, 116.1, 57.3, 21.2, 20.1.

Elemental analysis: Calcd for $C_{60}H_{53}F_{12}N_4O_{8.5}$ (**6**·0.3$H_2O$): C, 73.94; H, 5.35; N, 5.39. Found: C, 73.81; H, 5.45; N, 5.45.

**Scheme S5.** Synthesis of **8**[S6]




**7** **8**

A 100 mL three-necked round-bottom flask was charged with NaH (60%, 0.773 g, 19.3 mmol). The flask was evacuated then refilled with argon. Dry DMF (10 mL) was added to the flask. The flask was on an ice bath then dry DMF (25 mL) solution of **7**[S7] (1.84 g, 7.99 mmol) was added and the mixture was stirred under argon for 20 min. Chloromethyl methyl ether (1.80 mL, 23.7 mmol) was added and stirred at room temperature for 14 h. Sat. $NaHCO_3$aq (15 mL) was added, and the mixture was extracted with ethyl acetate / hexane (1:4) (50 mL × 3). The combined organic layer was washed with water (100 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude was purified by column chromatography on silica gel using ethyl acetate / hexane (1:8) as the eluent to give **8** (1.73 g, 5.96 mmol, 75%).

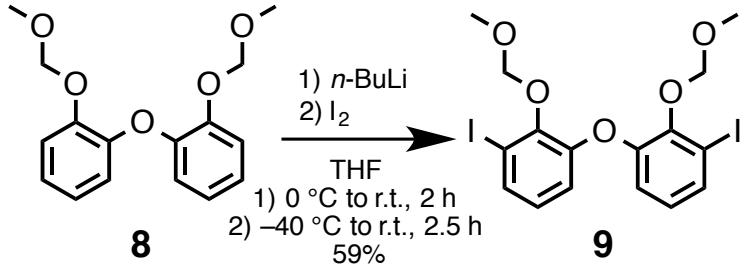
**8**: colorless oil;

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.21 (dd, $J$ = 8.0, 1.5 Hz, 2H), 7.04 (ddd, $J$ = 8.0, 7.7 1.5 Hz, 2H), 6.94 (ddd, $J$ = 8.0, 7.7, 1.5 Hz, 2H), 6.86 (dd, $J$ = 8.0, 1.5 Hz, 2H), 5.21 (s, 4H), 3.45 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 147.9, 147.0, 123.9, 122.6, 119.3, 117.5, 95.4, 56.2.

HRMS. Calcd for $C_{16}H_{18}O_5Na$ [**8**·Na]$^+$: *m/z* 313.1051 Found: *m/z* 313.1050.

**Scheme S6.** Synthesis of **9**




A 300 mL three-necked round-bottom flask was charged with **8** (2.05 g, 7.06 mmol). The flask was evacuated then refilled with argon. Dry THF (70 mL) was added to the flask. The flask was cooled in an ice bath then *n*-BuLi/*n*-Hexane (2.65 M, 6.20 mL, 16.4 mmol) was added and stirred in an ice bath for 5 min and at room temperature for 2 h. After cooled to –40 °C, the dry THF (20 mL) solution of $I_2$ (5.36 g, 21.1 mmol) was added and the mixture was stirred under argon at –40 °C for 15 min and at room temperature for 2.5 h. Sat. $Na_2SO_3$aq (70 mL) and brine (50 mL) was added and the mixture was extracted with ethyl acetate (50 mL × 3). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude was purified by column chromatography on silica using dichloromethane / *n*-hexane (1:1) as the eluent to give **9** (2.26 g, 4.17 mmol, 59%)

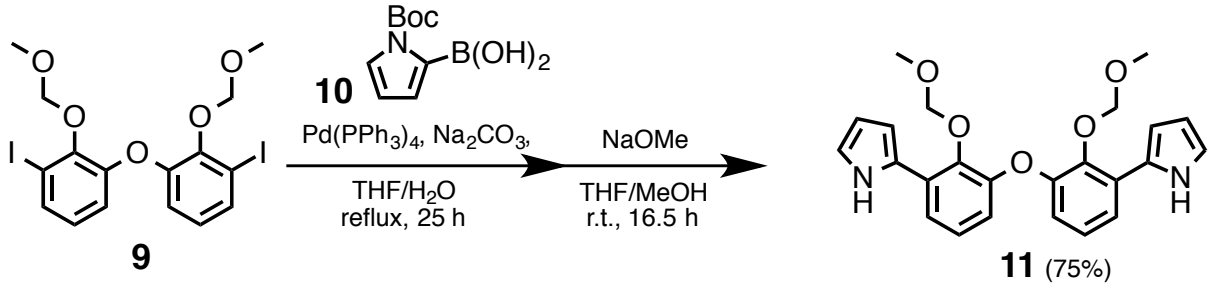
**9**: yellow oil;

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, $J$ = 7.9, 1.7 Hz, 2H), 6.83 (dd, $J$ = 7.9, 1.7 Hz, 2H), 6.78 (dd, $J$ = 7.9, 7.9 Hz, 2H), 5.22 (s, 4H), 3.61 (s, 6H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 149.0, 147.9, 134.5, 126.2, 120.0, 99.3, 93.2, 58.3

HRMS. Calcd for $C_{16}H_{16}O_5I_2Na$ [**9**·Na]$^+$: *m/z* 564.8984 Found: *m/z* 564.8979.

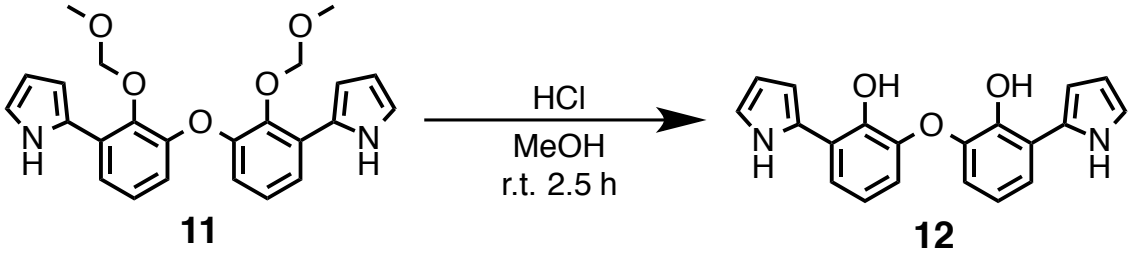
**Scheme S7.** Synthesis of **11**




A 200 mL three-necked round-bottom flask was charged with **9** (2.23 g, 4.11 mmol), **10**[S8] (3.55 g, 16.8 mmol), $Na_2CO_3$ (1.31 g, 12.4 mmol), and tetrakis(triphenylphosphine)palladium (0.146 g, 0.126 mmol). The flask was evacuated then refilled with argon. Dry THF (45 mL) and degassed water (15 mL) were added to the flask. The mixture was refluxed under argon for 25 h. After cooling, brine (50 mL) was added, and the mixture was extracted with ethyl acetate (50 mL × 3). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude was dissolved in dry THF (30 mL) in a 200 mL round-bottom flask, and the mixture of 28% NaOMe/MeOH (4.77 g, 24.7 mmol) and dry THF (30 mL) was added. The mixture was stirred under argon at room temperature for 16.5 h. Water (50 mL) and brine (50 mL) were added, and the mixture was extracted with ethyl acetate (50 mL × 3). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude was purified by column chromatography on silica gel using ethyl acetate / *n*-hexane (1:4) as the eluent to give **11** (1.30 g, 3.09 mmol, 75%).

**11**: pale purple solid;
m.p. 109–111 °C.
$^1$H NMR (400 MHz, $CDCl_3$) δ 9.99 (br, 2H), 7.39 (dd, $J$ = 8.0, 1.5 Hz, 2H), 7.04 (dd, $J$ = 8.0 Hz, 2H), 6.91–6.89 (m, 2H), 6.72 (dd, $J$ = 8.0, 1.5 Hz, 2H), 6.63–6.61 (m, 2H), 6.31–6.29 (m, 2H), 5.25 (s, 4H), 3.40 (s, 6H).
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 149.6, 143.2, 128.7, 127.6, 125.0, 122.4, 118.8, 116.6, 109.1, 107.6, 99.9, 58.0.
HRMS. Calcd for $C_{24}H_{24}N_2O_5Na$ [**11**·Na]$^+$: *m/z* 443.1582 Found: *m/z* 443.1587.

**Scheme S8.** Synthesis of **12**



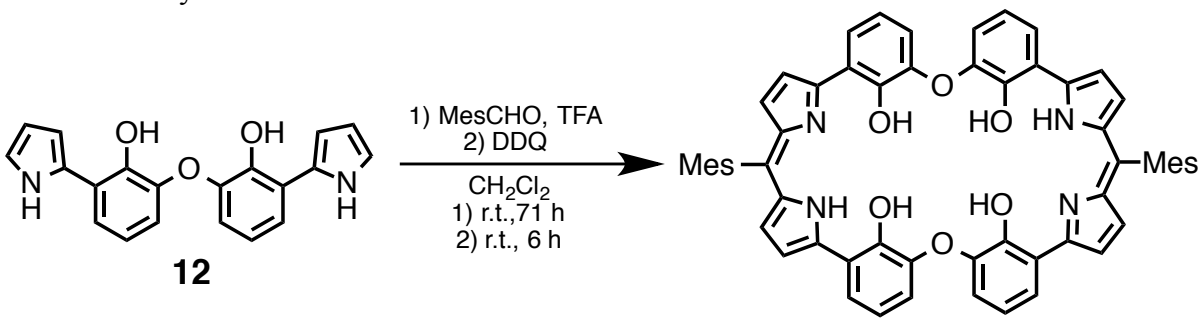

**11** **12**

A 500 mL round-bottom flask was charged with **11** (0.701 g, 1.67 mmol). The solid was dissolved in methanol (170 mL), and conc. HCl (17 mL) was added to the flask at 0 °C. The mixture was stirred at room temperature in the dark for 2.5 h. Sat. $NaHCO_3$aq (180 mL) was added. The mixture was stirred at room temperature for 10 min and extracted with chloroform (50 mL × 3). The combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo to give **12** (0.610 g), which was used for the next reaction without further purification.

**12**: pale green solid;

$^1$H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 2H), 7.44 (dd, $J$ = 8.0, 1.4 Hz, 2H), 6.93 (q, $J$ = 2.0 Hz, 2H), 6.87 (t, $J$ = 8.0 Hz, 2H), 6.71-6.67 (m, 4H), 6.33 (q, $J$ = 3.1 Hz, 2H), 6.21 (d, $J$ = 0.6 Hz, 2H).

**Scheme S9.** Synthesis of **13**




**13** (11% from **11**)

A 500 mL round-bottom flask was charged with **12** (0.610 g), 2,4,6-trimethylbenzaldehyde (0.248 g, 1.67 mmol) and degassed dichloromethane (160 mL). The solution was deoxygenated by vacuum–Ar cycles. Trifluoroacetic acid (0.129 mL, 1.67 mmol) was added and the mixture was stirred under argon at room temperature in the dark for 71 h. DDQ (0.382 g, 1.68 mmol) was added and the mixture was stirred under argon at room temperature in the dark for another 6 h. Triethylamine (0.326 mL, 2.34 mmol) was added and the reaction mixture was loaded onto a short alumina-gel column and eluted with ethyl acetate. Eluted bands were collected and concentrated in vacuo, which was purified by column chromatography on silica gel (eluent: $CHCl_3$) and GPC using chloroform to give **13** (84.0 mg, 0.0912 mmol, 11% in 2 steps from **11**).

**13**: dark red solid;

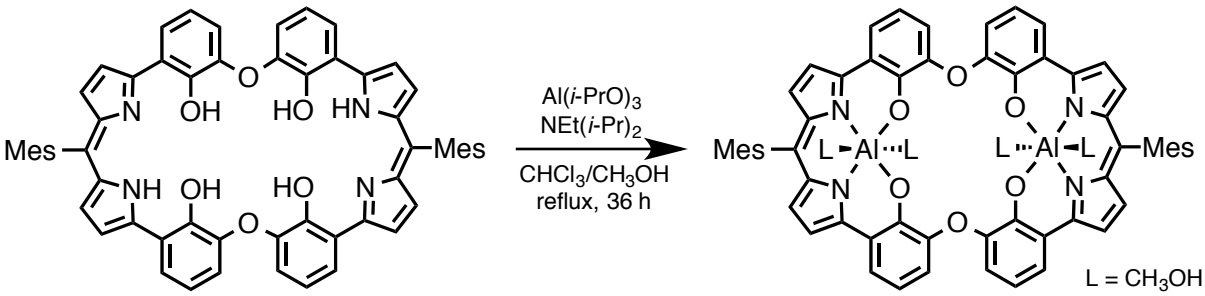
m.p. > 280 °C.

$^1$H NMR (400 MHz, $CDCl_3$) δ 12.84 (br, 2H), 7.50 (dd, $J$ = 7.6, 1.8 Hz, 4H), 6.96 (s, 4H), 6.92–6.85 (m, 12H), 6.53 (d, $J$ = 4.4 Hz, 4H), 4.78 (br, 4H), 2.38 (s, 6H), 2.14 (s, 12H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 153.7, 147.7, 144.2, 139.1, 139.1, 137.7, 137.1, 134.4, 128.9, 127.9, 122.7, 119.5, 119.4, 117.9, 115.9, 21.2, 20.0.

Elemental analysis: Calcd for $C_{60}H_{53}F_{12}N_4O_{8.5}$ (**13**·2.5$H_2O$): C, 74.59; H, 5.53; N, 5.80. Found: C, 74.68; H, 5.30; N, 5.92.

**Scheme S10.** Synthesis of ALDIPY dimer [**2**·$(CH_3OH)_4$]




**13** [**2**·$(CH_3OH)_4$] (37%)

A round-bottom flask was charged with **13** (15.3 mg, 0.0166 mmol) and aluminum triisopropoxide (7.44 mg, 0.0364 mmol). Chloroform (16 mL), methanol (8 mL), and *N*,*N*-diisopropylethylamine (0.017 mL, 0.010 mmol) were added to the flask. The mixture was refluxed for 36 h. After cooling, the solution was concentrated in vacuo. The crude was purified by column chromatography on alumina gel (eluent: $CHCl_3$ : methanol = 100 : 0 ~ 100 : 1) to give [**2**·$(CH_3OH)_4$] (6.7 mg, 0.00611 mmol, 37%).

[**2**·$(CH_3OH)_4$]: blue solid;

m.p. >280 °C.

$^1$H NMR (600 MHz, $CDCl_3$/$CD_3OD$ = 4:1 (v/v)) δ 7.41 (d, *J* = 8.0 Hz, 4H), 7.06 (d, J = 7.6 Hz, 4H), 6.98 (s, 4H), 6.89 (d, *J* = 4.2 Hz, 4H), 6.61 (dd, *J* = 8.0, 7.6 Hz, 4H), 6.57 (d, *J* = 4.2 Hz, 4H), 2.40 (s, 6H), 2.19 (br, 12H).

$^{13}$C NMR (151 MHz, $CDCl_3$/$CD_3OD$ = 4:1 (v/v)) δ 157.9, 153.8, 146.5, 140.8, 140.6, 137.5, 137.0, 134.6, 129.9, 128.0, 121.8, 121.3, 116.8, 115.5, 115.3, 21.2, 20.0.

Elemental analysis: Calcd for $C_{64.5}H_{60.5}Al_2Cl_{1.5}N_4O_{11}$ ([**2**·$(CH_3OH)_4$·$H_2O$·0.5$CHCl_3$]: C, 65.94; H, 5.19; N, 4.77. Found: C, 65.63; H, 5.00; N, 4.93.

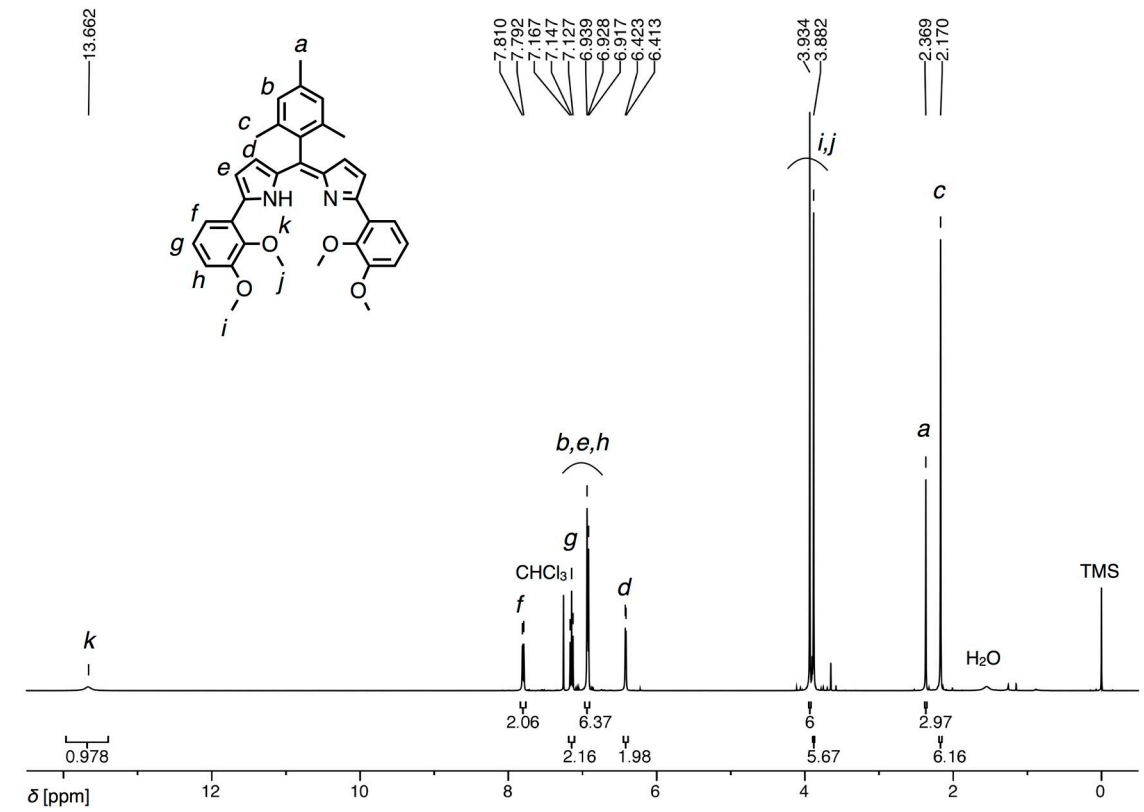



**Figure S1.** $^{1}$H NMR spectrum of **5** (400 MHz, $CDCl_3$).

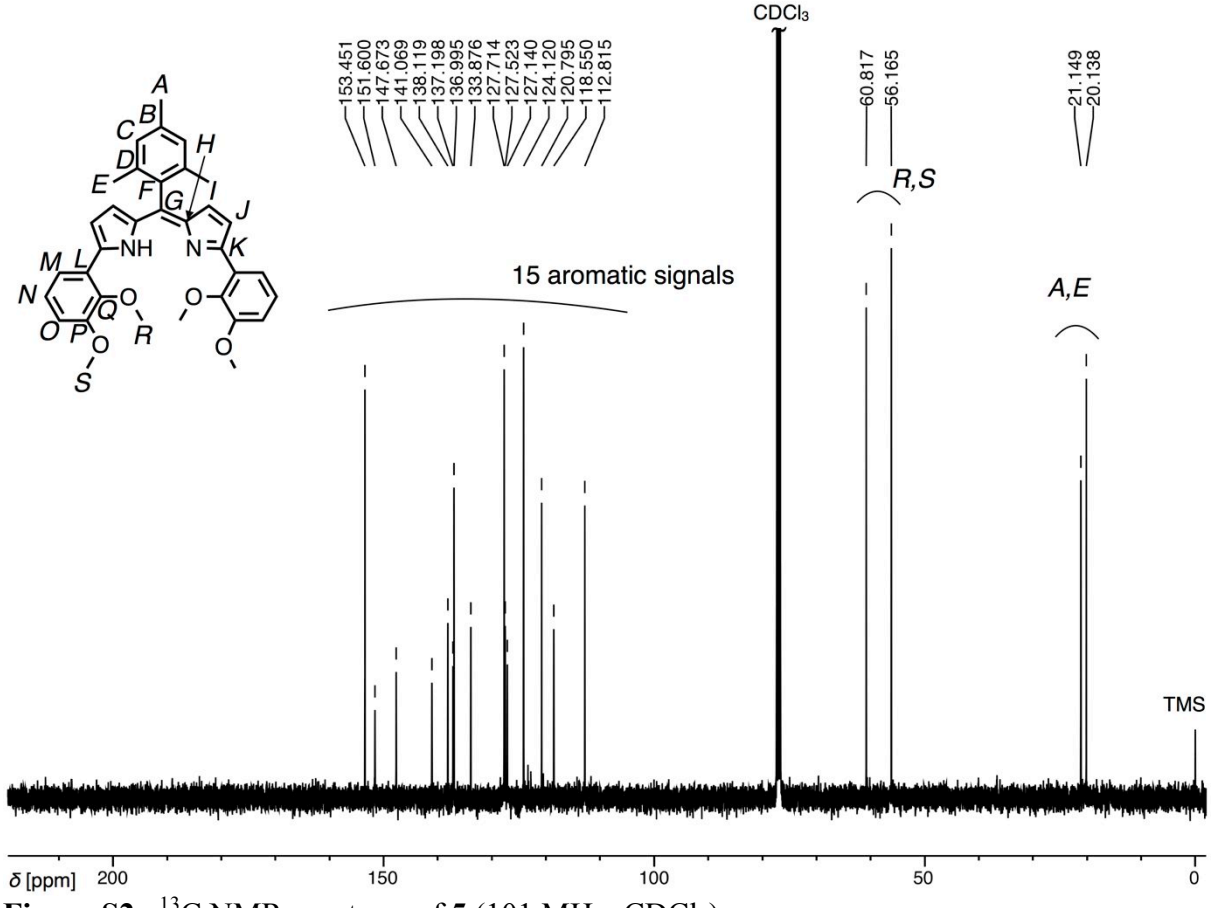



**Figure S2.** $^{13}$C NMR spectrum of **5** (101 MHz, $CDCl_3$).

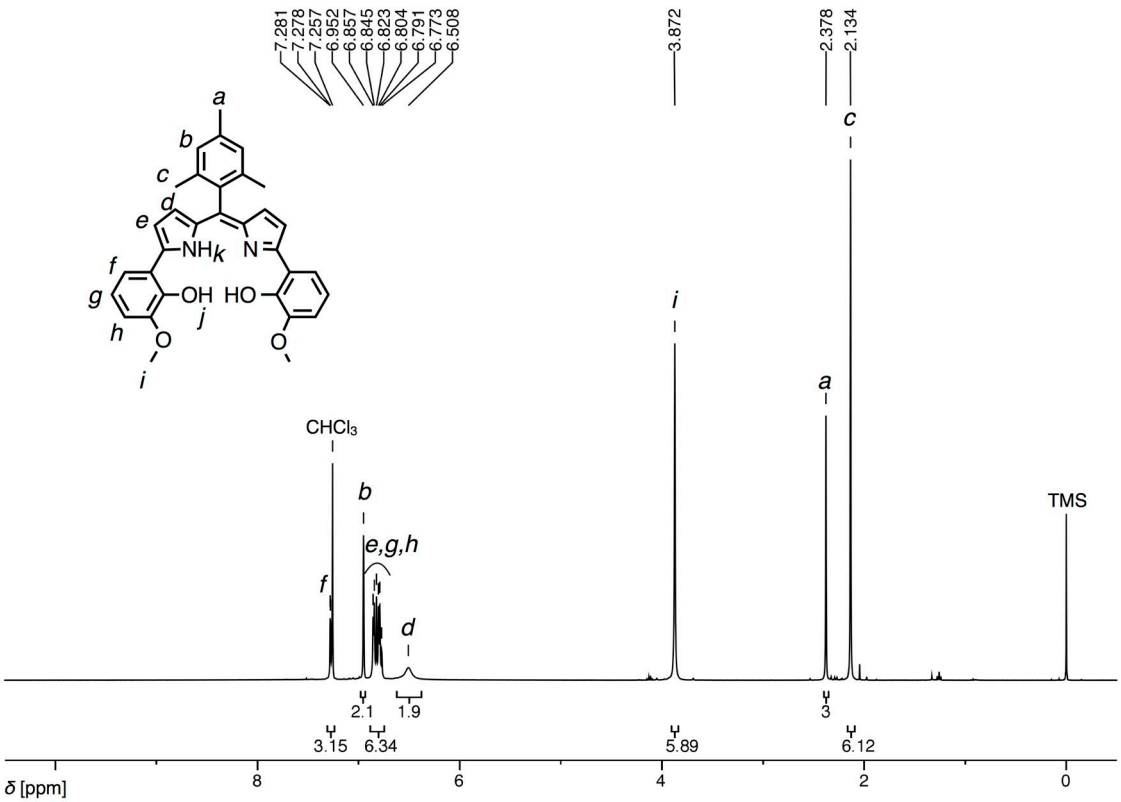



**Figure S3.** $^{1}$H NMR spectrum of **6** (400 MHz, $CDCl_3$).

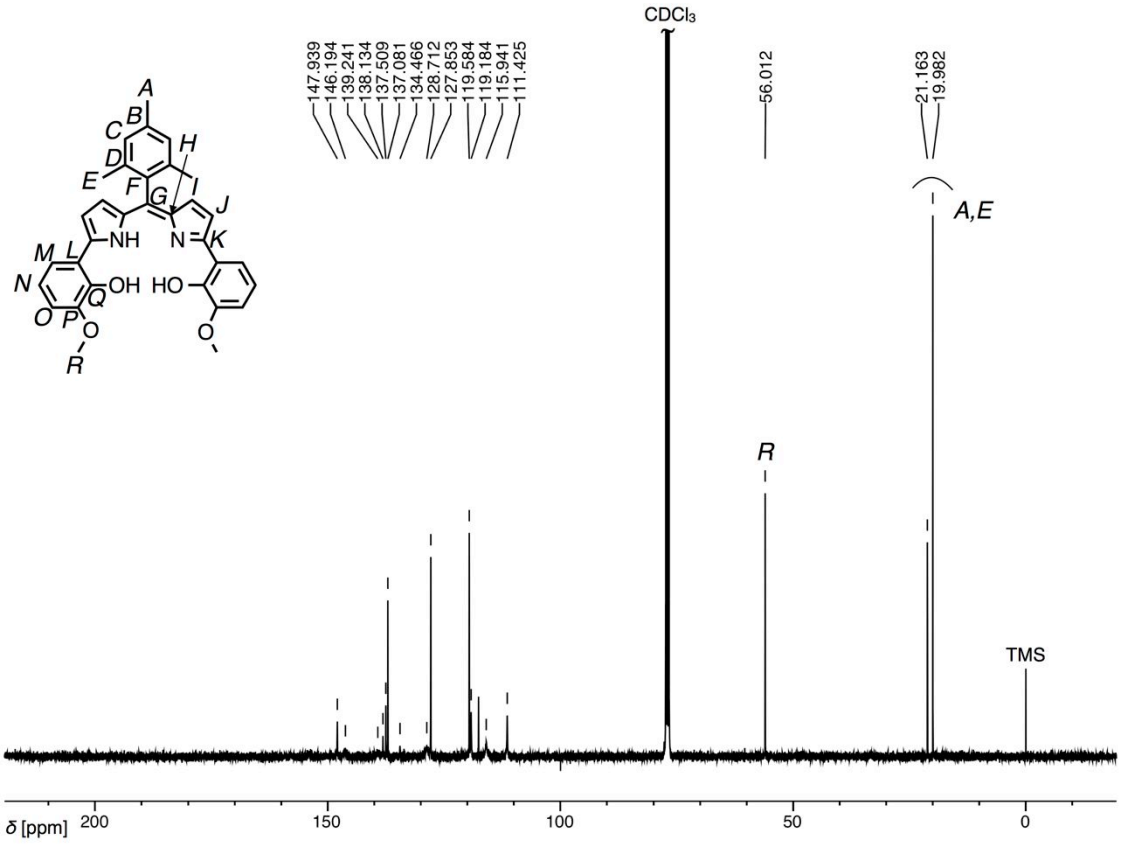



**Figure S4.** $^{13}$C NMR spectrum of **6** (101 MHz, $CDCl_3$).

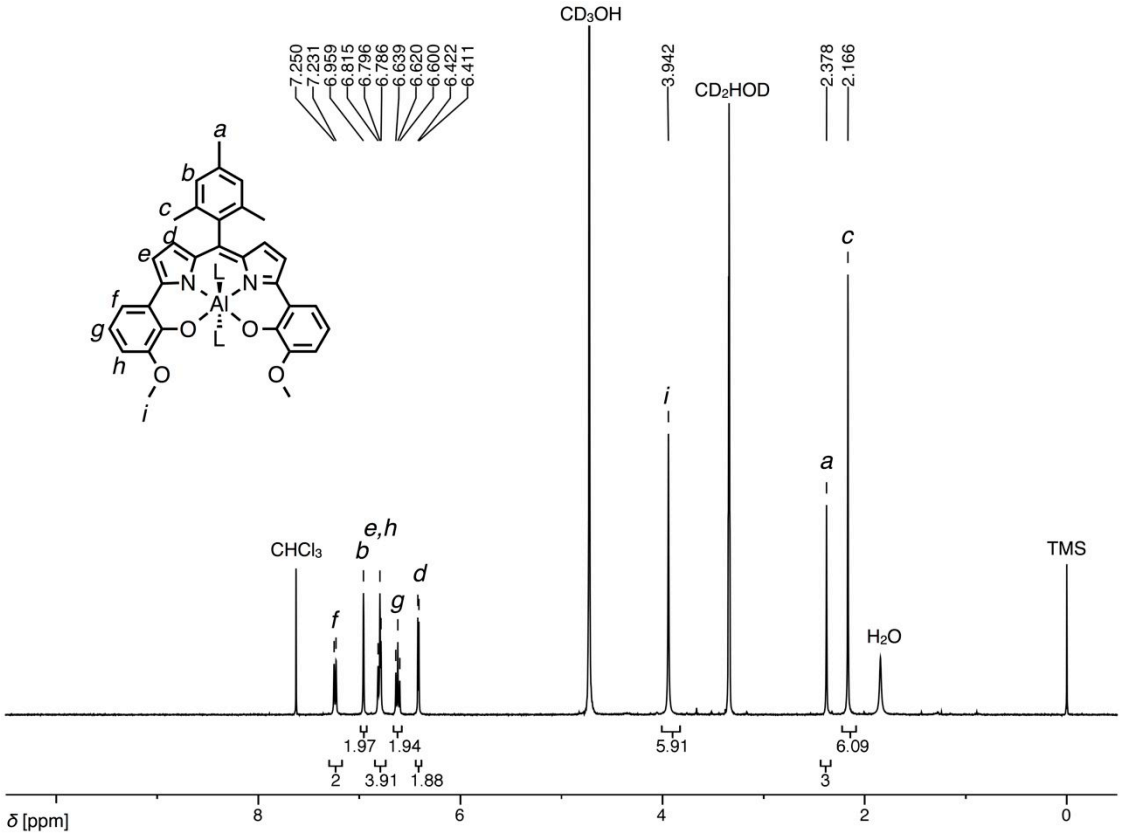



**Figure S5.** $^{1}$H NMR spectrum of [**1**·$L_2$] (400 MHz, $CDCl_3$/$CD_3OD$ = 1:1).

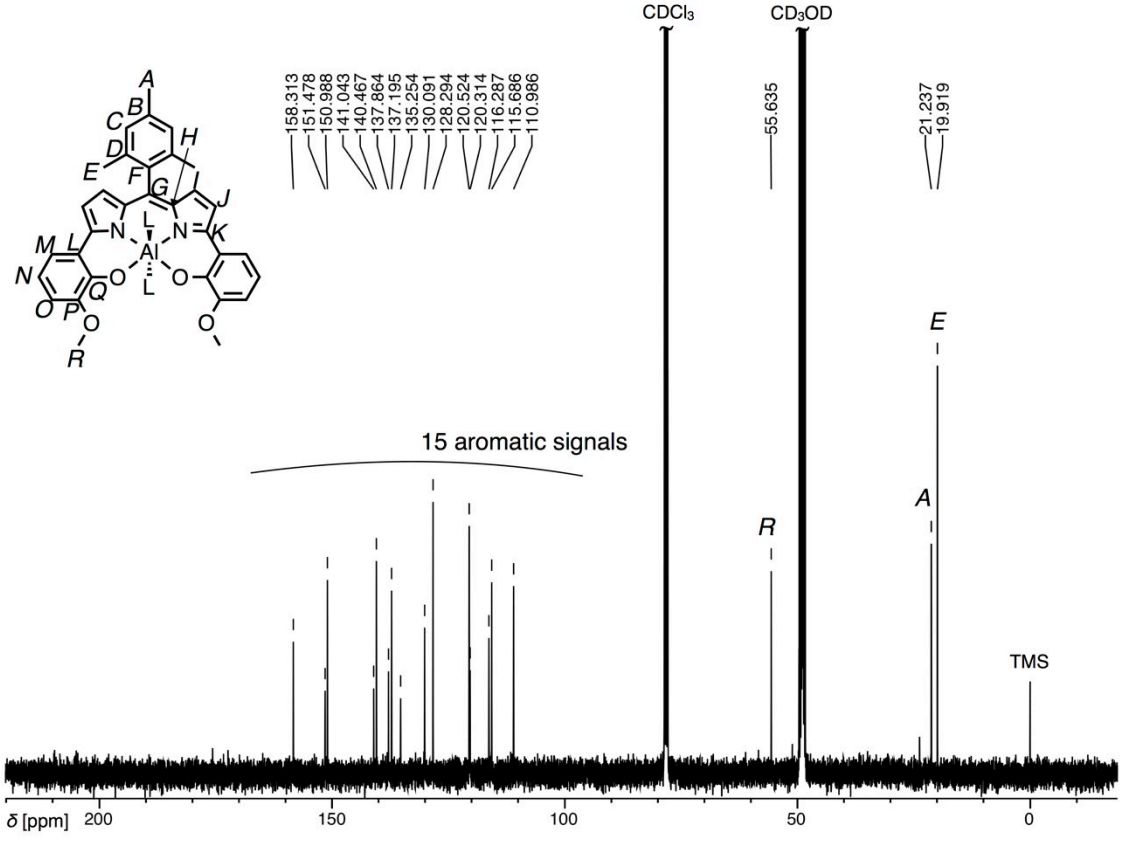



**Figure S6.** $^{13}$C NMR spectrum of [**1**·$L_2$] (101 MHz, $CDCl_3$).

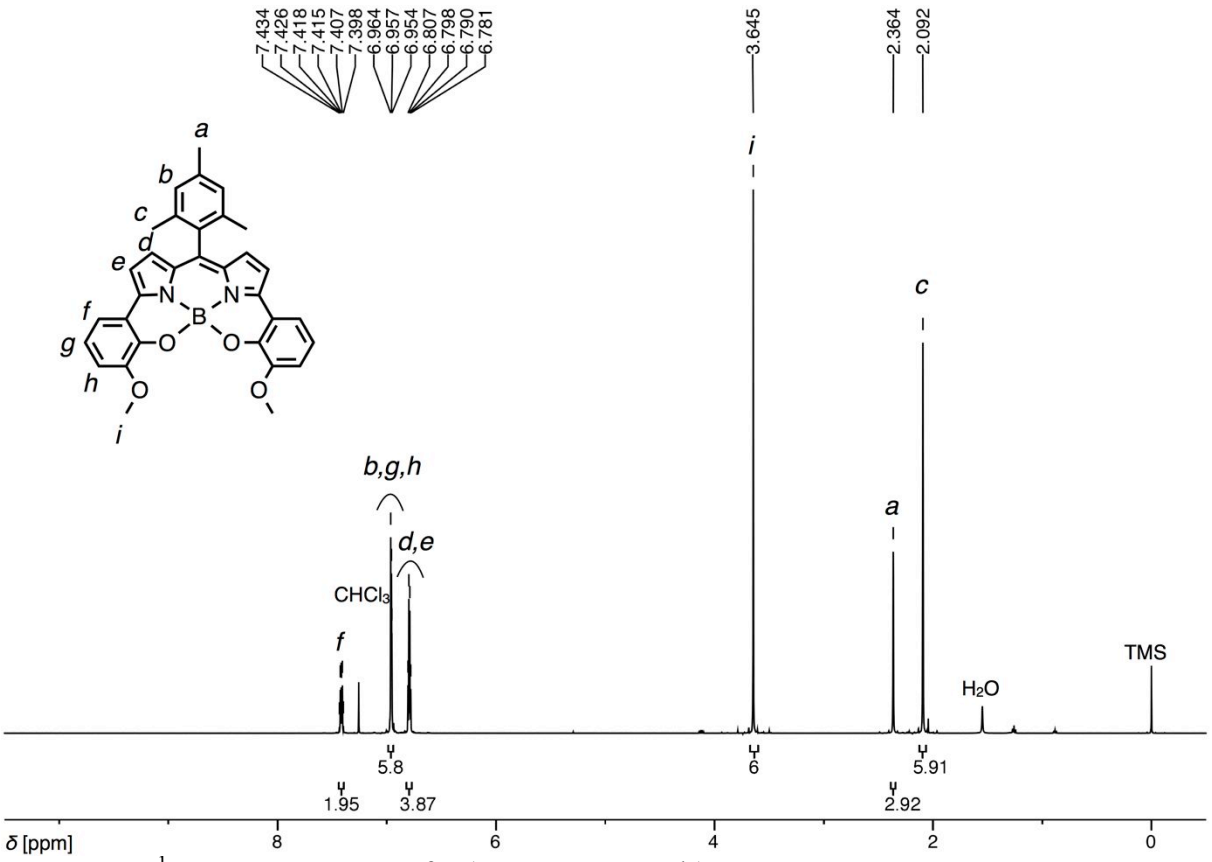



**Figure S7.** $^{1}$H NMR spectrum of **3** (500 MHz, $CDCl_3$).

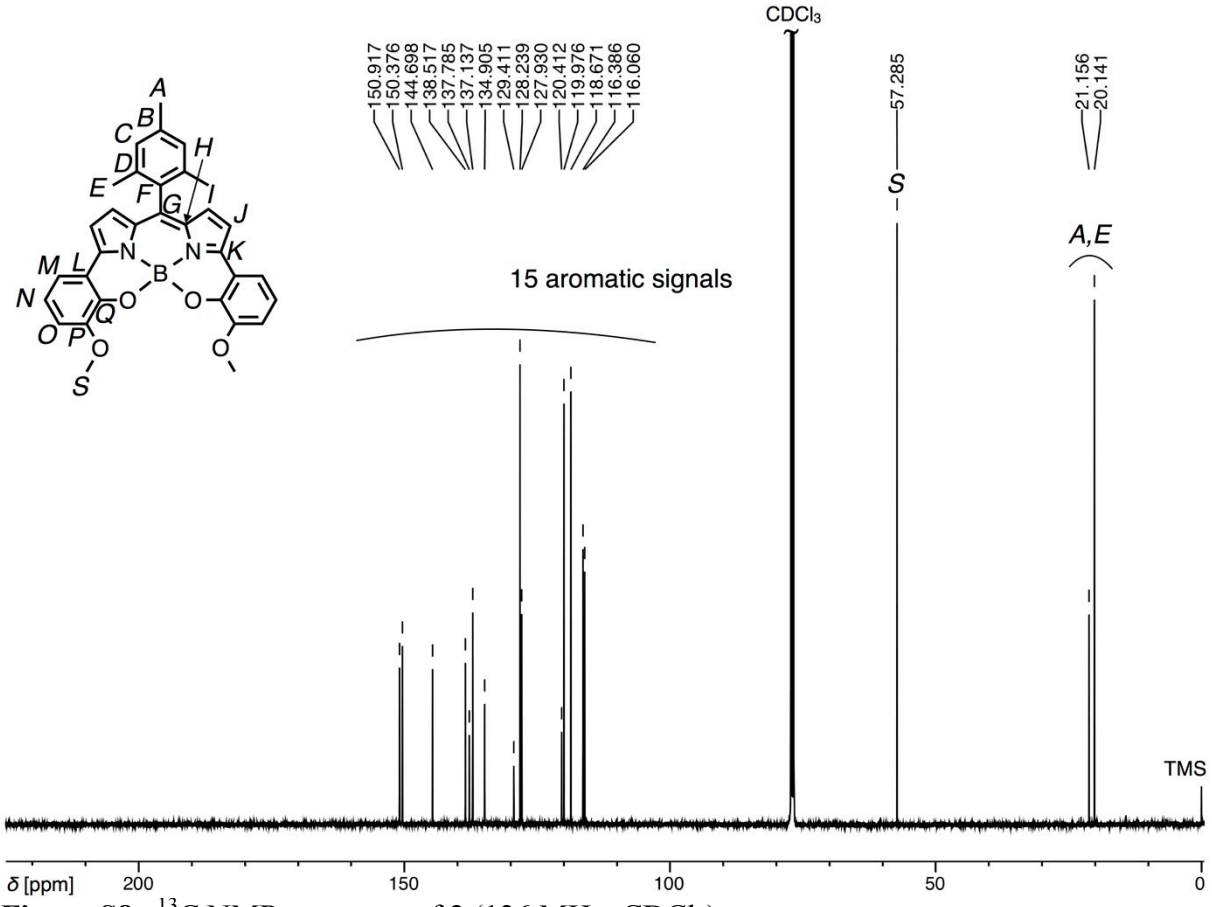



**Figure S8.** $^{13}$C NMR spectrum of **3** (126 MHz, $CDCl_3$).

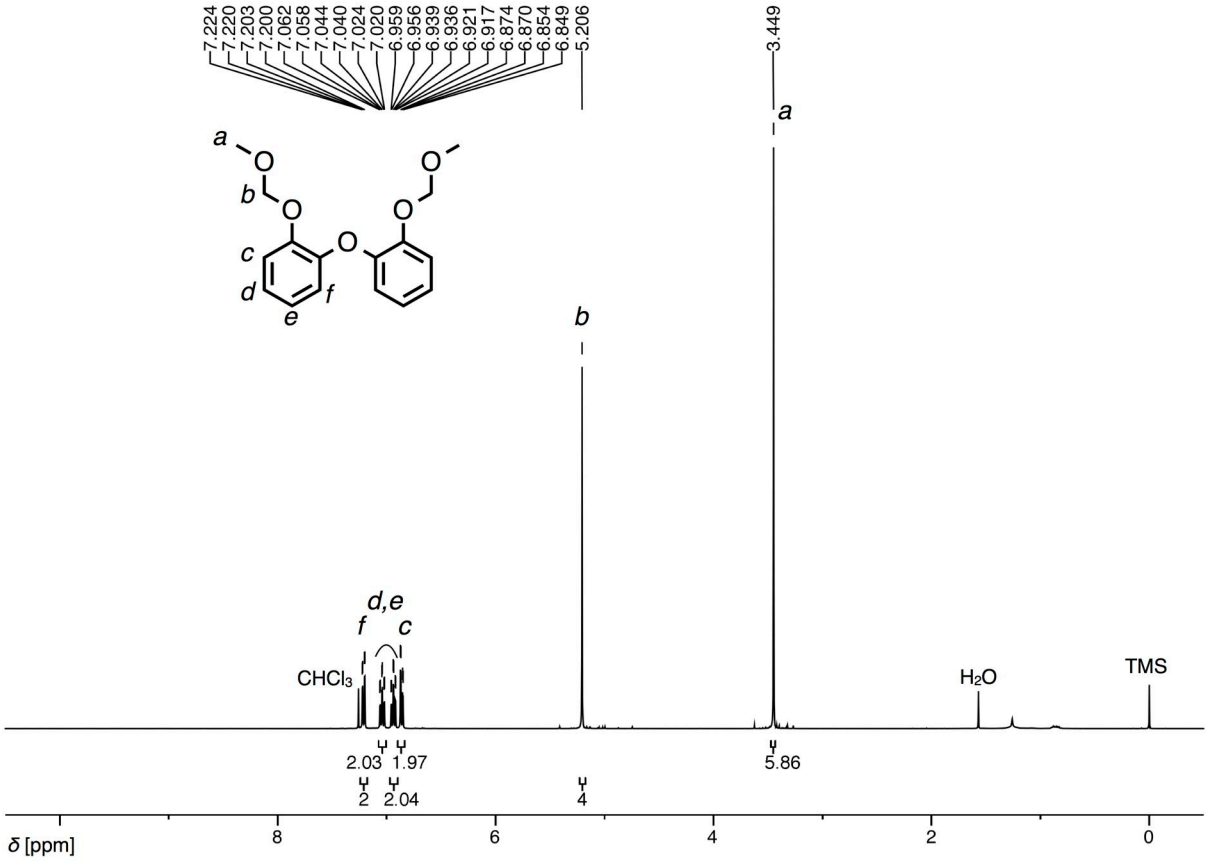



**Figure S9.** $^{1}$H NMR spectrum of **8** (400 MHz, $CDCl_3$).

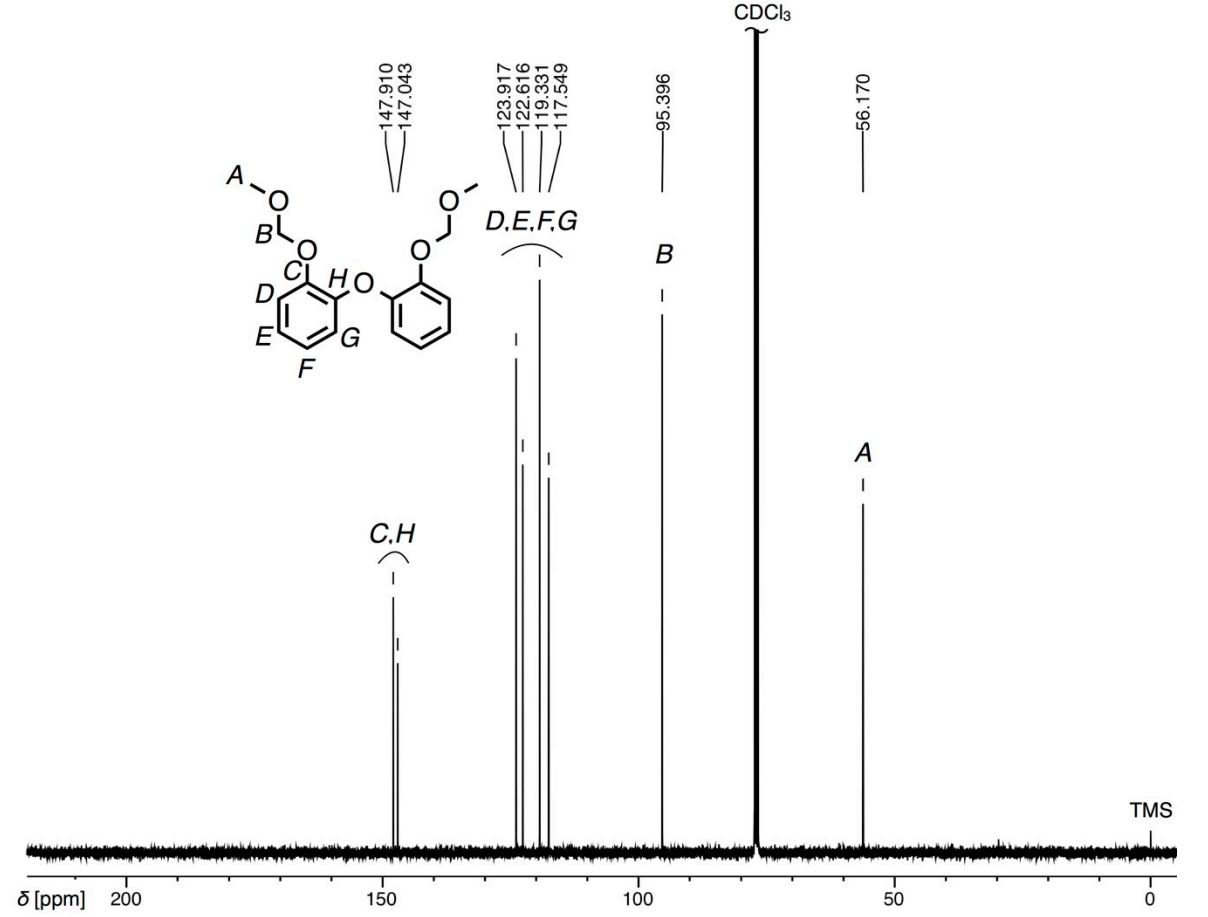



**Figure S10.** $^{13}$C NMR spectrum of **8** (101 MHz, $CDCl_3$).

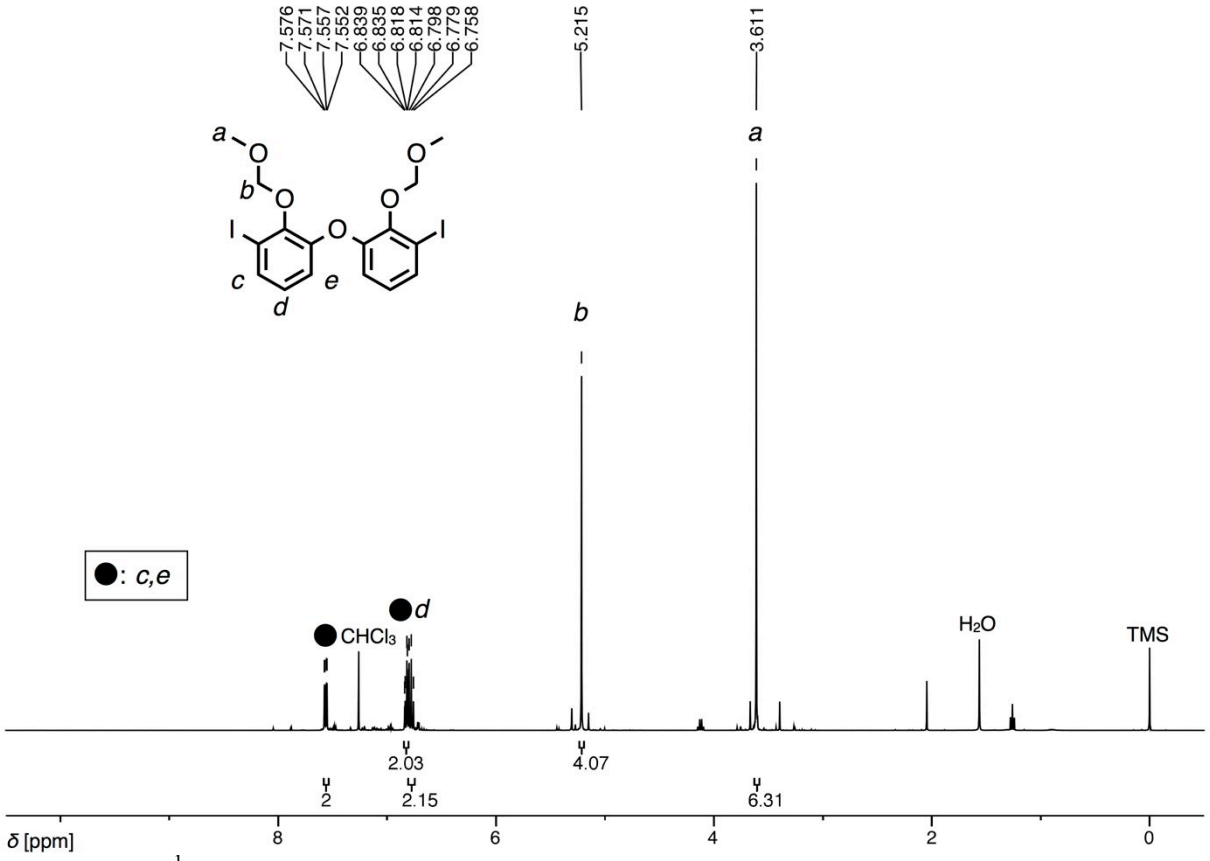



**Figure S11.** $^{1}$H NMR spectrum of **9** (400 MHz, $CDCl_3$).

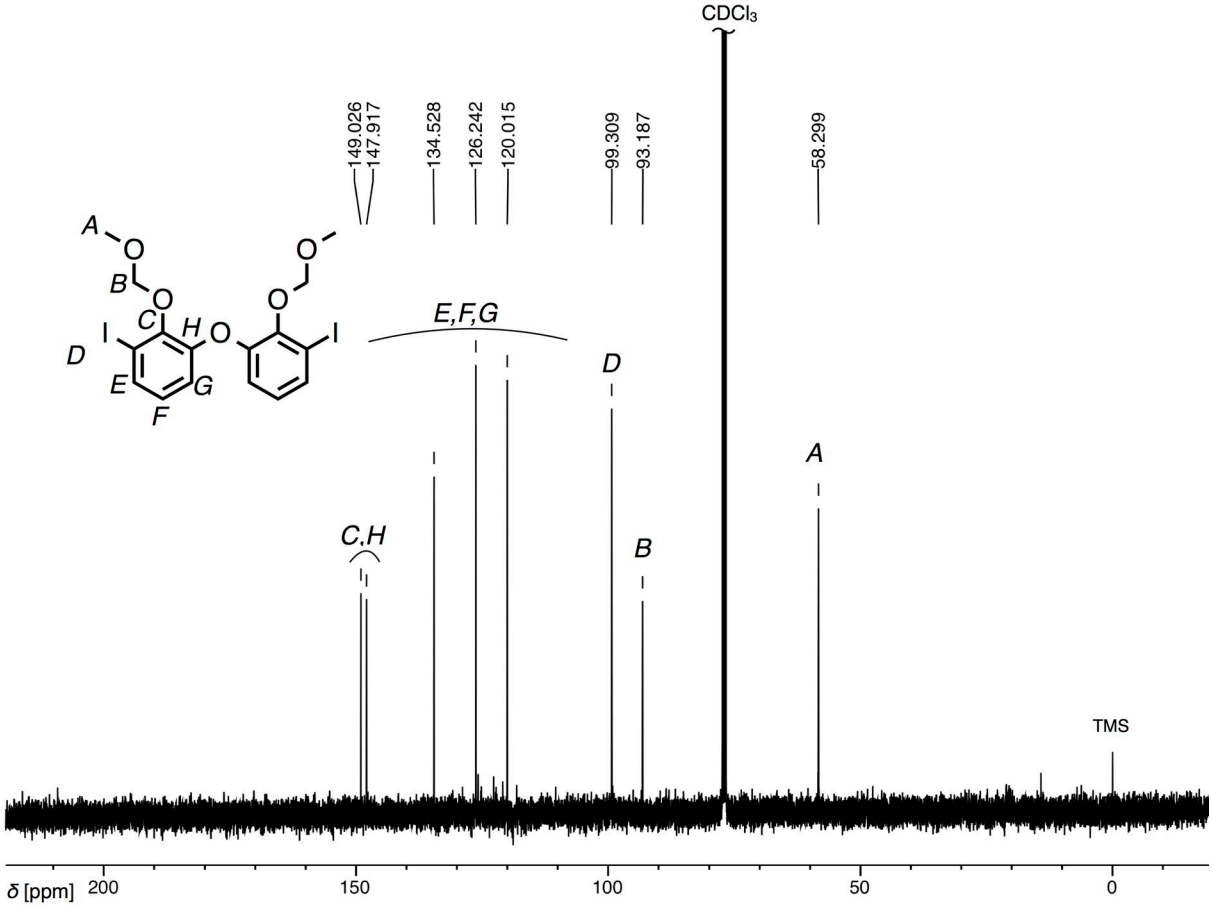



**Figure S12.** $^{13}$C NMR spectrum of **9** (101 MHz, $CDCl_3$).

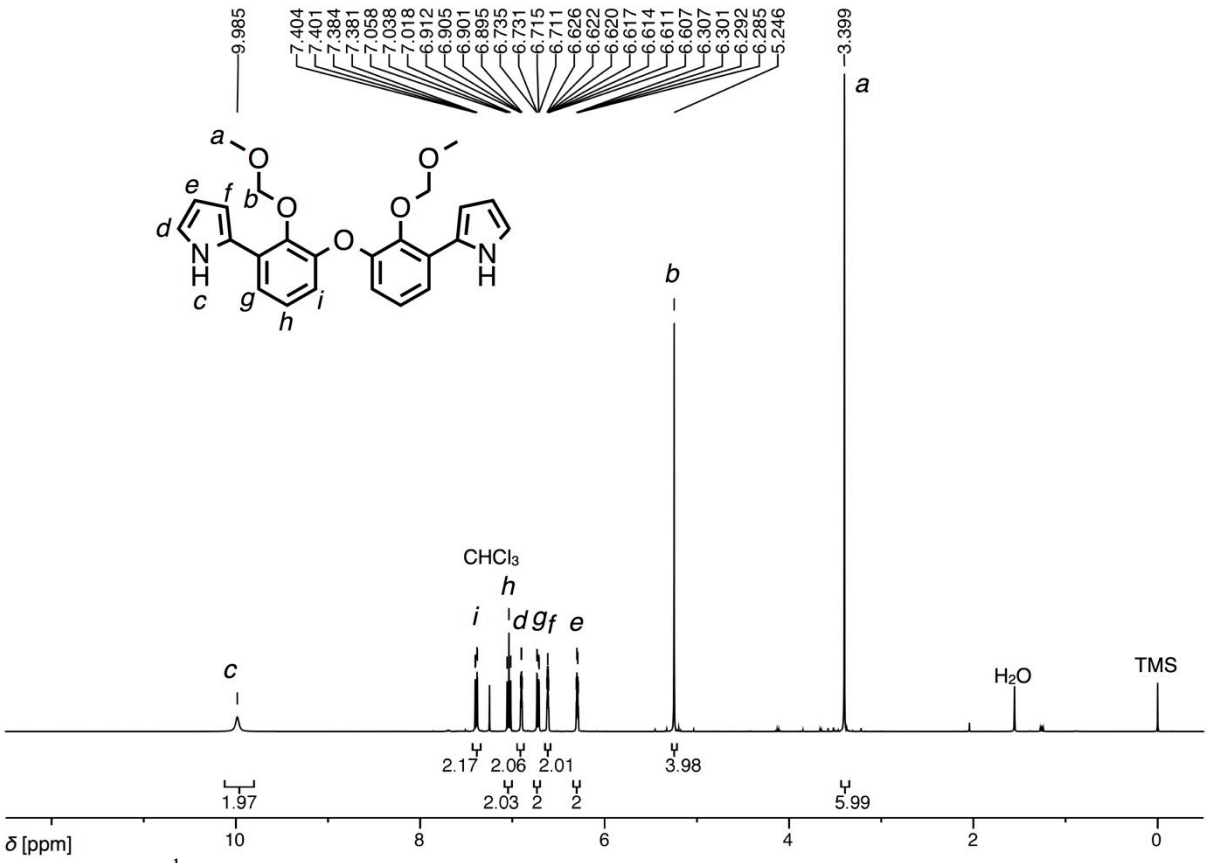



**Figure S13.** $^{1}$H NMR spectrum of **11** (400 MHz, $CDCl_3$).

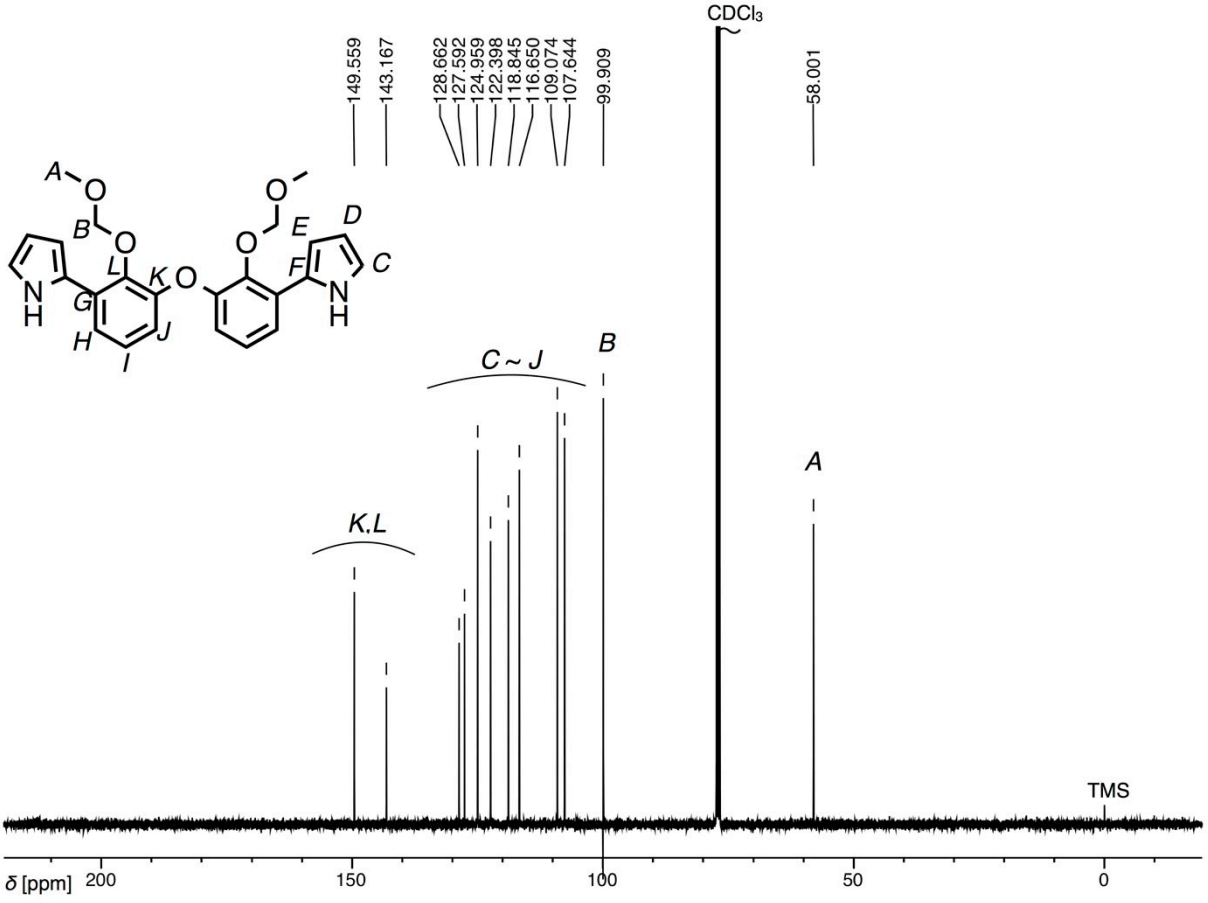



**Figure S14.** $^{13}$C NMR spectrum of **11** (101 MHz, $CDCl_3$).

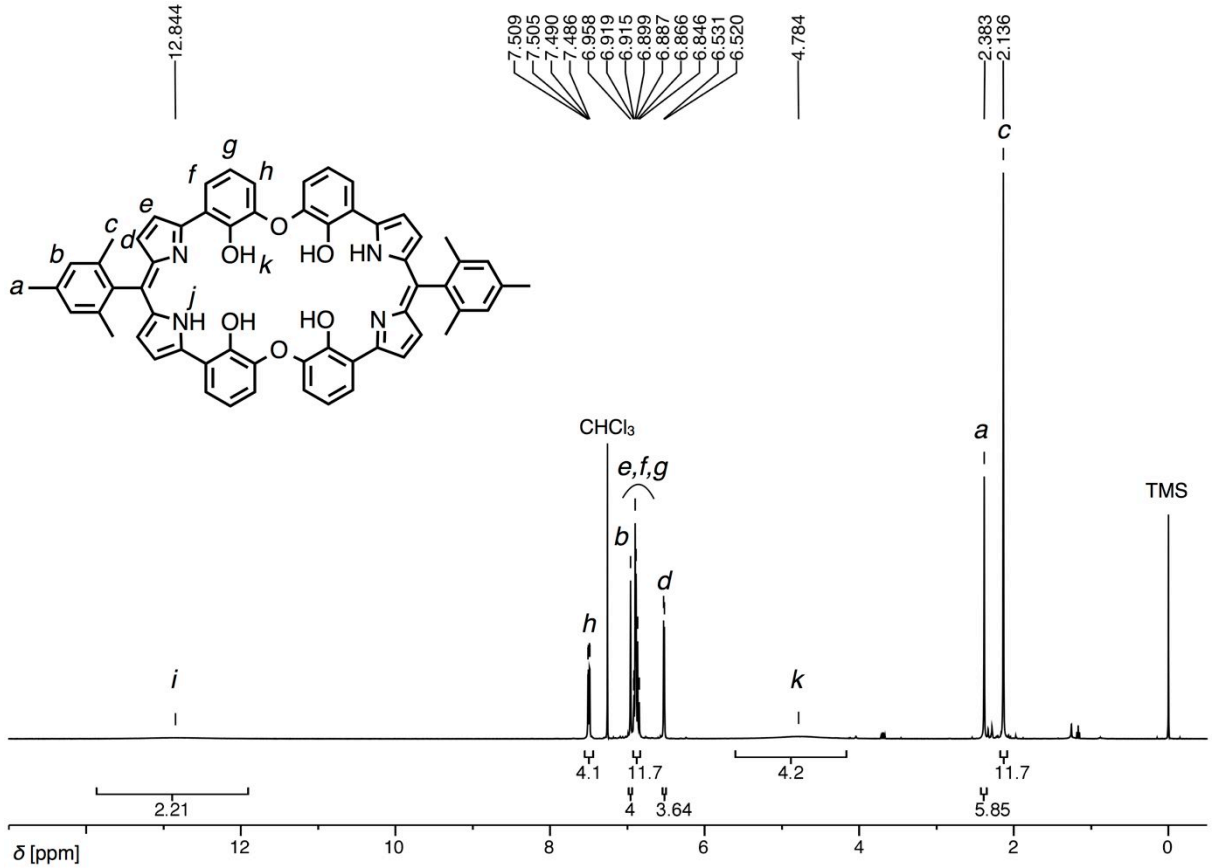



**Figure S15.** $^{1}$H NMR spectrum of **13** (400 MHz, $CDCl_3$).

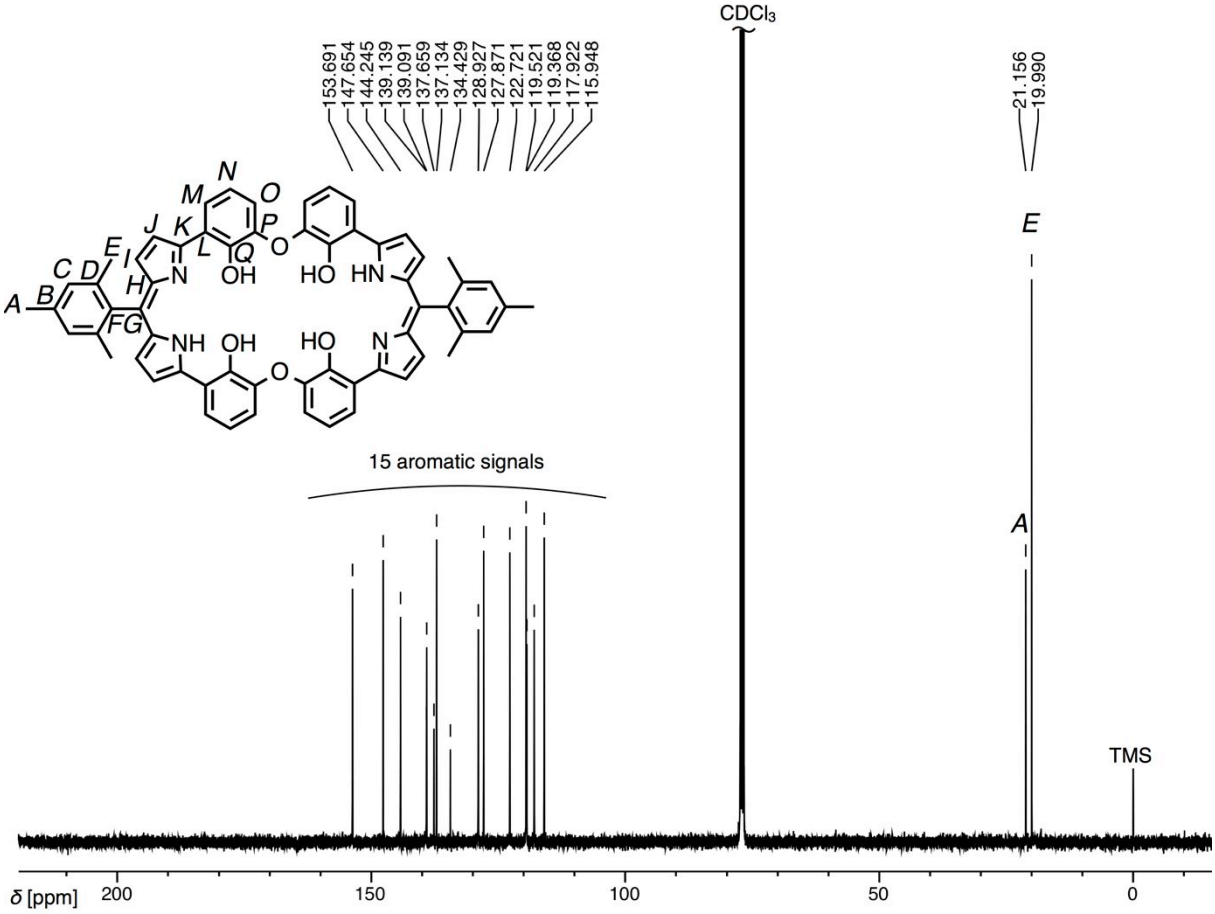



**Figure S16.** $^{13}$C NMR spectrum of **13** (101 MHz, $CDCl_3$).

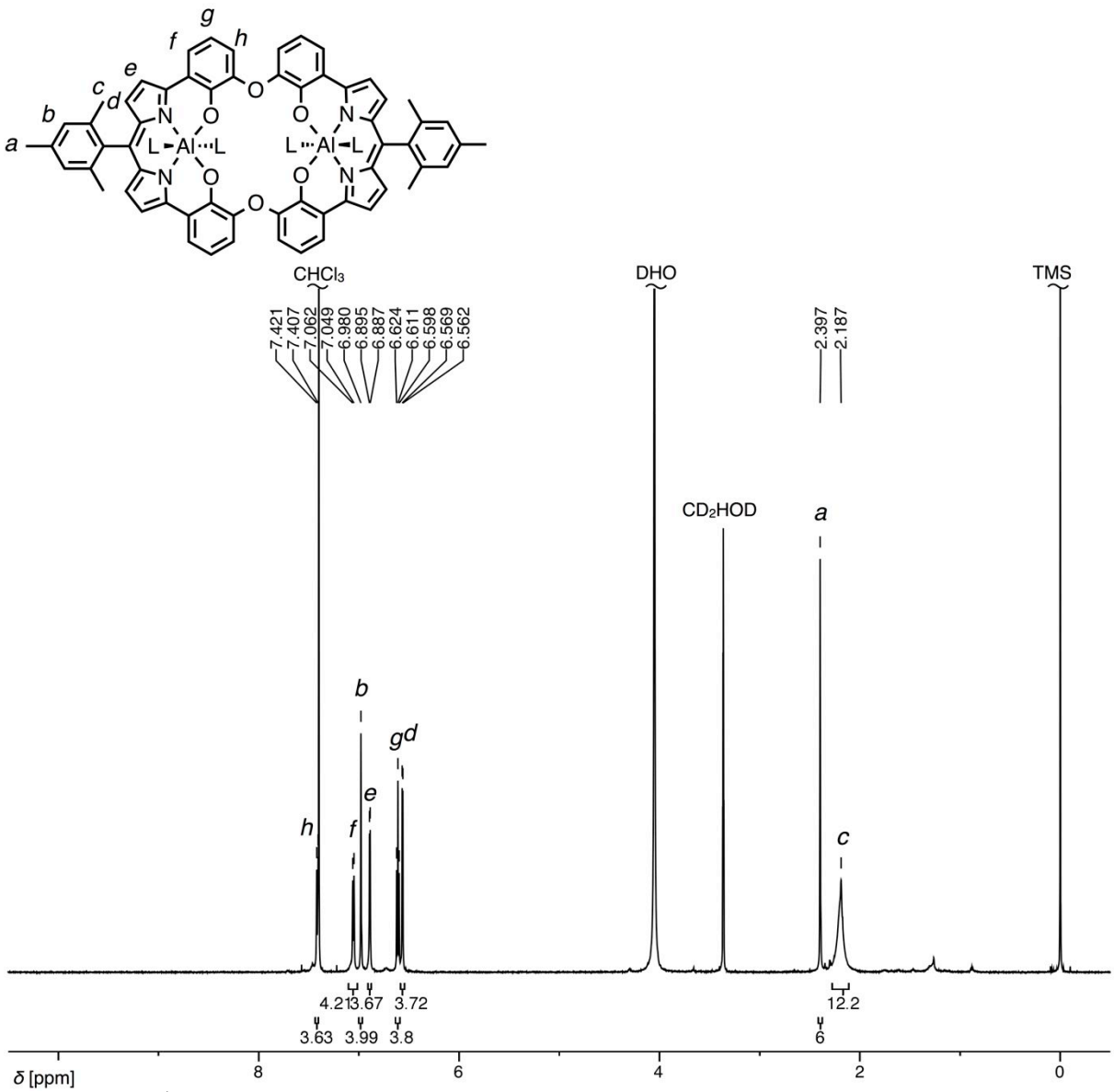



**Figure S17.** $^{1}$H NMR spectrum of [**2**·$L_4$] (600 MHz, $CDCl_3/CD_3OD$ = 4:1 (v/v)).

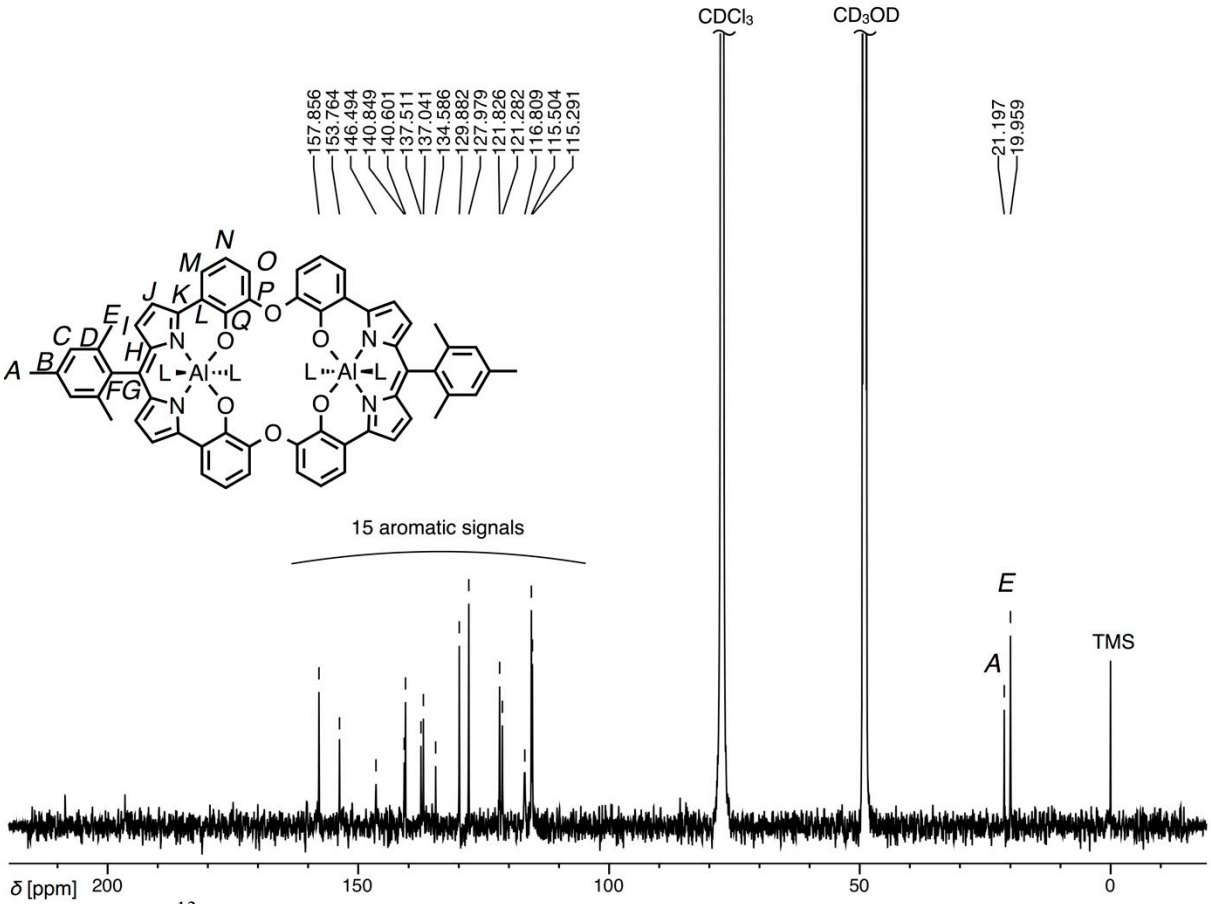



**Figure S18.** $^{13}$C NMR spectrum of [**2**·$L_4$] (151 MHz, $CDCl_3$/$CD_3OD$ = 4:1 (v/v)).

## X-ray crystallographic analysis

### X-ray crystallographic analysis of monomer ligand 6

Single crystal of **6** suitable for X-ray diffraction analysis was obtained by slow diffusion of *n*-hexane vapor into dichloromethane solution of **6**. All of the positional parameters and thermal parameters of non-hydrogen atoms were anisotropically refined on $F^2$ by the full-matrix least-squares method. Hydrogen atoms on carbon atoms were placed at the calculated positions and refined riding on their corresponding carbon atoms. Two hydrogen atoms on hydroxy groups and two on pyrrole groups were refined based on *d*-Fourier map. Two hydrogen atoms on the other two hydroxy groups were not located.

Crystal data for $\mathbf{6}_2$: $C_{64}H_{60}N_4O_8$, $Fw$ = 1013.16, purple plate, 0.47 × 0.15 × 0.04 mm$^3$, monoclinic, space group $P2_1/n$ (No. 14), $a$ = 13.3625(9) Å, $b$ = 13.7619(9) Å, $c$ = 28.7802(18) Å, $\beta$ = 90.967(3) Å, $V$ = 5291.7(6) Å$^3$, $Z$ = 4, $T$ = 120(2) K, $\lambda$(Mo$K\alpha$) = 0.71073 Å, $\theta_{max}$ = 30.544°, $R_1$ = 0.0969, $wR_2$ = 0.2529, GOF = 1.428. CCDC No.: 1446114.

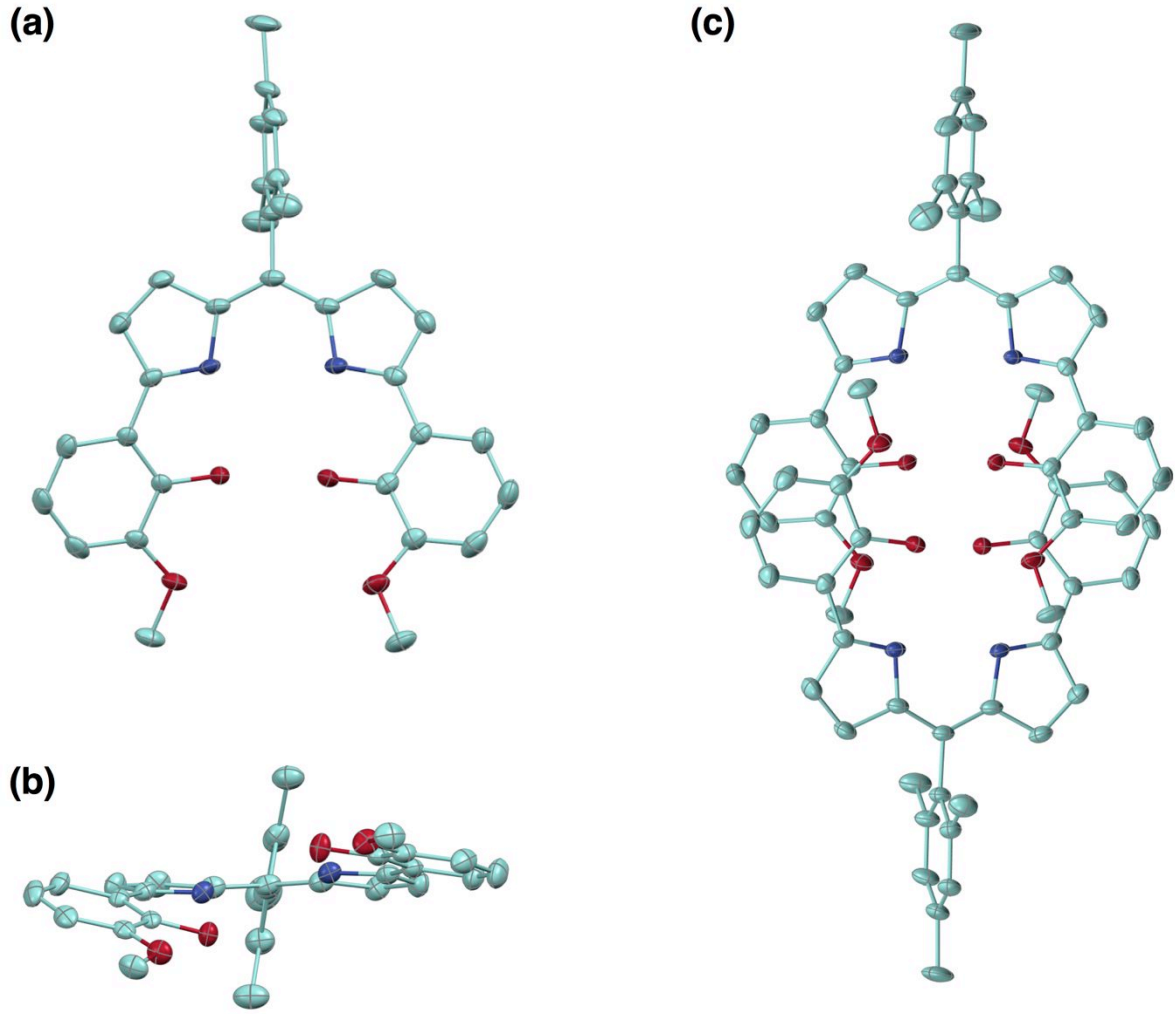



**Figure S19.** Crystal structure of **6**. An ellipsoidal model (50% probability). Hydrogen atoms were omitted for clarity. C, light green; N, blue; and O, red. (a) A top view. (b) A side view. (c) A dimeric structure in the crystal.

**X-ray crystallographic analysis of ALDIPY monomer [1·($CH_3OH$)($H_2O$)]**

Single crystal of [**1**·($CH_3OH$)($H_2O$)] suitable for X-ray diffraction analysis was obtained by slow evaporation of dichloromethane/methanol solution of [**1**·$\mathbf{L}_2$]. All of the positional parameters and thermal parameters of non-hydrogen atoms were anisotropically refined on $F^2$ by the full-matrix least-squares method. Hydrogen atoms on carbon atoms and a hydrogen on methanol solvent were placed at the calculated positions and refined riding on their corresponding atoms. Hydrogen atoms on water and a methanol coordinated to Al were refined based on *d*-Fourier map.

Crystal data for [**1**·($CH_3OH$)($H_2O$)]($CH_3OH$): $C_{34}H_{37}AlN_2O_7$, $Fw$ = 612.64, green block, 0.27 × 0.11 × 0.06 mm$^3$, triclinic, space group *P*-1 (No. 2), $a$ = 11.5013(5) Å, $b$ = 11.9173(5) Å, $c$ = 13.3035(6) Å, $\alpha$ = 102.745(2) Å, $\beta$ = 106.178(2) Å, $\gamma$ = 112.038(2) Å, $V$ = 1511.12(12) Å$^3$, $Z$ = 2, $T$ = 120(2) K, $\lambda$(Mo$K\alpha$) = 0.71073 Å, $\theta_{max}$ = 30.619°, $R_1$ = 0.0573, $wR_2$ = 0.1942, GOF = 1.164. CCDC No.: 1446110.

**X-ray crystallographic analysis of BODIPY monomer 3**

Single crystal of **3** suitable for X-ray diffraction analysis was obtained by slow liquid layer diffusion of *n*-hexane on dichloromethane solution of **3**. All of the positional parameters and thermal parameters of non-hydrogen atoms were anisotropically refined on $F^2$ by the full-matrix least-squares method. Hydrogen atoms on carbon atoms were placed at the calculated positions and refined riding on their corresponding atoms.

Crystal data for **3**: $C_{32}H_{27}BN_2O_4$, $Fw$ = 514.37, purple block, 0.18 × 0.17 × 0.12 mm$^3$, orthorhombic, space group *Pbca* (No. 60), $a$ = 17.1558(6) Å, $b$ = 11.8814(4) Å, $c$ = 24.8691(8) Å, $V$ = 5069.2(3) Å$^3$, $Z$ = 8, $T$ = 120(2) K, $\lambda$(Mo$K\alpha$) = 0.71073 Å, $\theta_{max}$ = 30.518°, $R_1$ = 0.0518, $wR_2$ = 0.1700, GOF = 1.046. CCDC No.: 1446111.

**X-ray crystallographic analysis of a macrocyclic ligand 13**

Single crystal of **13** suitable for X-ray diffraction analysis was obtained by slow diffusion of hexane vapor in to a chloroform solution of **13**. All of the positional parameters and thermal parameters of non-hydrogen atoms were anisotropically refined on $F^2$ by the full-matrix least-squares method. Solvent accessible voids of 2831 cubic angstroms were found, where solvent molecules (chloroform and hexane) were heavily disordered. The electron densities in the voids were treated by the SQUEEZE program. Hydrogen atoms on phenoxy oxygens and methyl groups were refined based on *d*-Fourier map. Hydrogen atoms of the water in the macrocyclic framework of **13** were not located. The other Hydrogen atoms were placed at the calculated positions and refined riding on their corresponding atoms.

Crystal data for **13**$_2$·2$H_2O$: $C_{120}H_{100}N_8O_{12}$, $Fw$ = 1846.07, monoclinic, space group *C2/c* (No. 15), $a$ = 23.498(4) Å, $b$ = 38.393(7) Å, $c$ = 23.360(4) Å, $\beta$ = 91.080(3) Å, $V$ = 21071(6) Å$^3$, $Z$ = 8, $T$ = 120(2) K, $\lambda$(Mo$K\alpha$) = 0.71073 Å, $\theta_{max}$ = 24.850°, $R_1$ = 0.0623, $wR_2$ = 0.1857 (after SQUEEZE), GOF = 1.107. CCDC No.: 1446113.

**X-ray crystallographic analysis of ALDIPY dimer [2·($CH_3OH$)$_4$·(OH)·Na]**

Single crystal of [**2**·($CH_3OH$)$_4$·(OH)·Na] suitable for X-ray diffraction analysis was obtained by slow evaporation of chloroform/methanol solution of [**2**·$L_4$]. All of the positional parameters and thermal parameters of non-hydrogen atoms were anisotropically refined on $F^2$ by the full-matrix least-squares method. Hydrogen atoms on carbon atoms were placed at the calculated positions and refined riding on their corresponding atoms.

Hydrogen atoms of methanol coordinated to Al were not located. Since disordered solvent molecules in the crystal were not able to be fully determined, it cannot be concluded whether the deprotonation of $CH_3OH$ / $H_2O$ took place or a counter anion existed in the void of the crystal.

Crystal data for [**2**·$(CH_3OH)_4$·(OH)·Na]: $C_{64}H_{59}Al_2N_4NaO_{11}$, $Fw$ = 1137.1, monoclinic, space group *C2/c* (No. 15), $a$ = 24.6207(14) Å, $b$ = 7.271(3) Å, $c$ = 35.445(6) Å, $\beta$ = 111.987(3) Å, $V$ = 5884(3) Å$^3$, $Z$ = 4, $T$ = 100(2) K, $\lambda$(Mo$K\alpha$) = 0.71073 Å, $\theta_{max}$ = 27.604°, $R_1$ = 0.1208, $wR_2$ = 0.3923, GOF = 1.314. CCDC No.: 1446112.

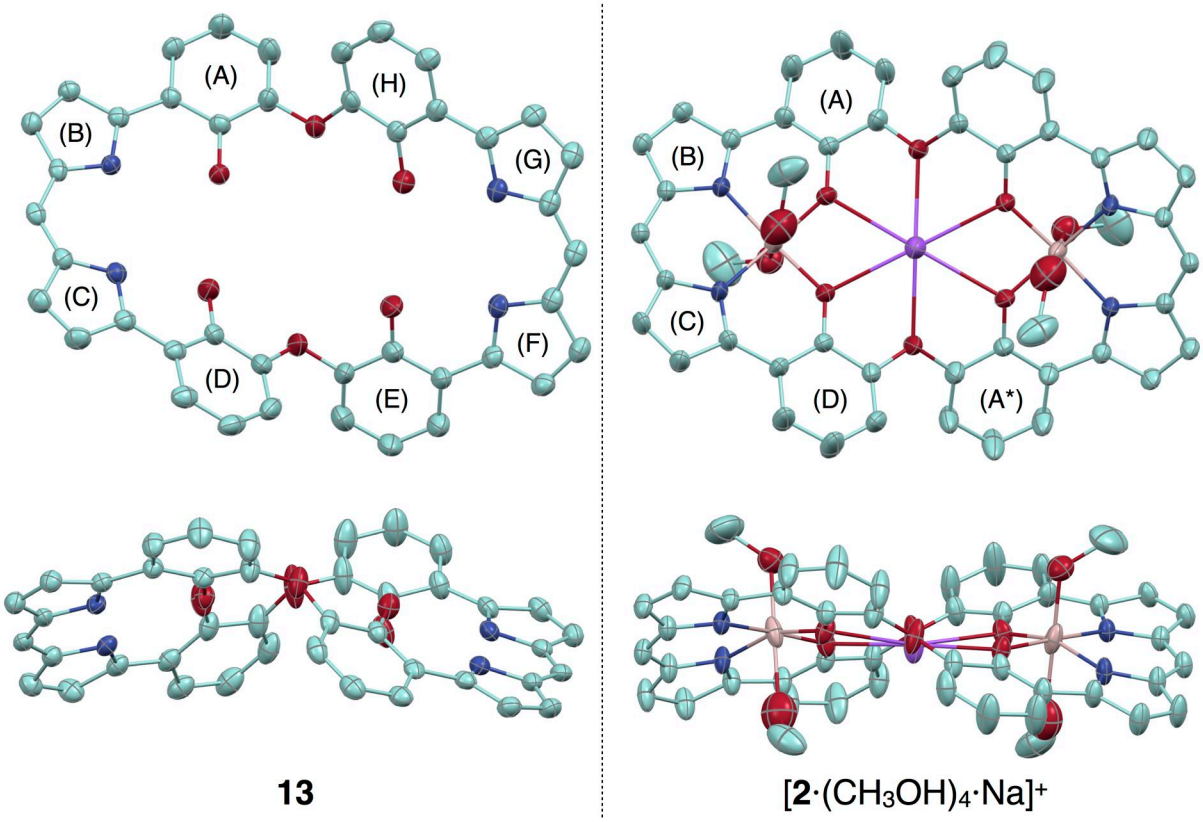



**Table S1.** Dihedral angles between aromatic rings of a macrocyclic ligand **13** and a host–guest complex of ALDIPY dimer and $Na^+$ ion, [**2**·$(CH_3OH)_4$·Na]$^+$. The asymmetric unit of crystal contained two molecules of **13**, and one of the structures (**13**$_{(1)}$) was shown above.

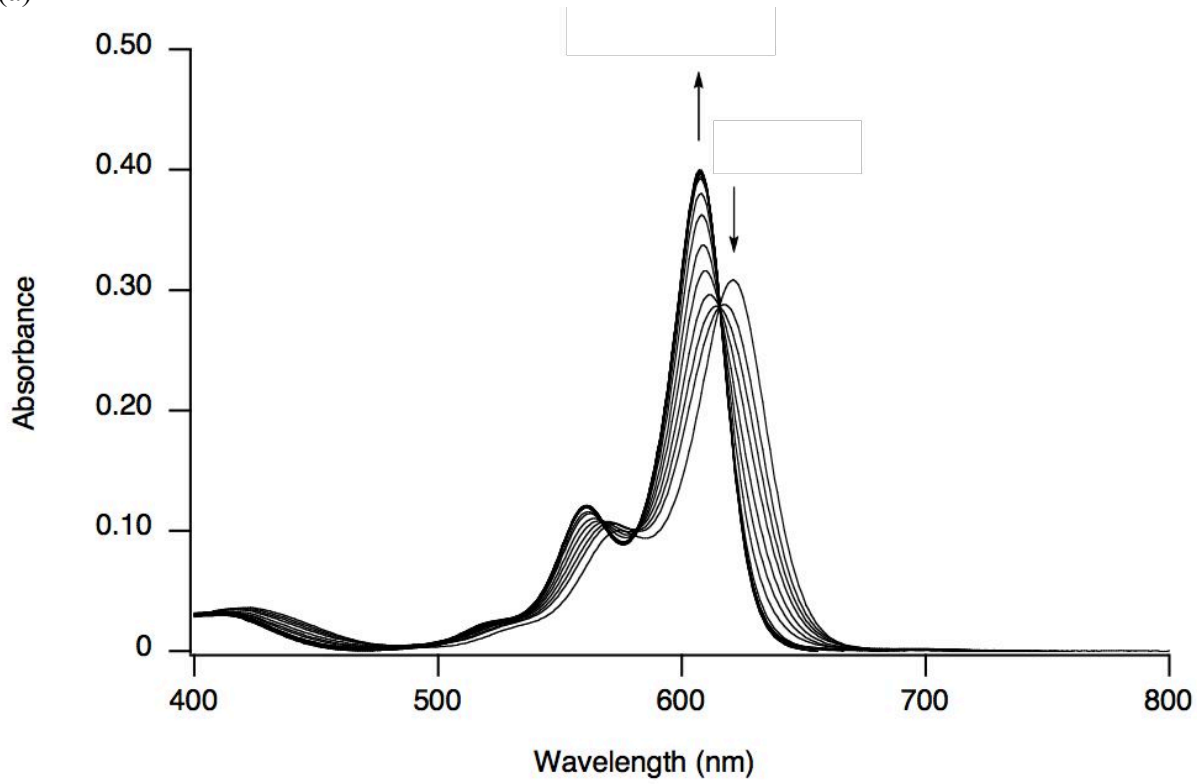
| **13** | | | [**2**·$(CH_3OH)_4$·Na]$^+$ | |
|---|---|---|---|---|
| | **13**$_{(1)}$ | **13**$_{(2)}$ | | |
| (A)–(B) | 14.8° | 9.6° | (A)–(B) | 12.8° |
| (B)–(C) | 7.2° | 7.2° | (B)–(C) | 10.4° |
| (C)–(D) | 17.0° | 10.3° | (C)–(D) | 1.6° |
| (D)–(E) | 77.0° | 82.0° | (D)–(A*) | 52.9° |
| (E)–(F) | 10.6° | 18.3° | – | – |
| (F)–(G) | 6.4° | 8.8° | – | – |
| (G)–(H) | 10.2° | 15.4° | – | – |
| (H)–(A) | 63.4° | 67.9° | – | – |

**Recognition of alkaline earth ions**

**A representative procedure.**

In a 5 mL vial, 1740 μM MeOH solution of $Ca(ClO_4)_2$ (100 μL, 0.174 μmol) was added and concentrated to dryness. Here, 5.0 μM $CH_3OH/H_2O/CHCl_3$ = 89.5:10:0.5 (v/v/v) solution of ALDIPY dimer [**2**·$L_4$] (1400 μL) was added, which gave 124 μM $CH_3OH/H_2O/CHCl_3$ stock solution of $Ca(ClO_4)_2$ (solution A). In a 5 mL vial, 1740 μM MeOH solution of $Ca(ClO_4)_2$ (600 μL, 1.044 μmol) was placed and concentrated to dryness. Here, 5.0 μM $CH_3OH/H_2O/CHCl_3$ = 89.5:10:0.5 (v/v/v) solution of ALDIPY dimer [**2**·$L_4$] (1000 μL) was added, which gave 1044 μM $CH_3OH/H_2O/CHCl_3$ stock solution of $Ca(ClO_4)_2$ (solution B). In an UV cell, 5.0 μM $CH_3OH/H_2O/CHCl_3$ = 89.5:10:0.5 (v/v/v) solution of ALDIPY dimer [**2**·$L_4$] (3000 μL, 15 nmol) was placed. The stock solution was titrated into the sample solution (solution A, $[Ca^{2+}]/[\mathbf{2}]$ = 0–2.0 eq; solution B, > 2.0 eq ) and UV/Vis absorption measurements were performed. Each measurement was performed in about 30 seconds after each addition of stock solution. The association constant was determined by the least square fitting of 1:1 binding model using the TitrationFit software[S9].

(a)




(b)

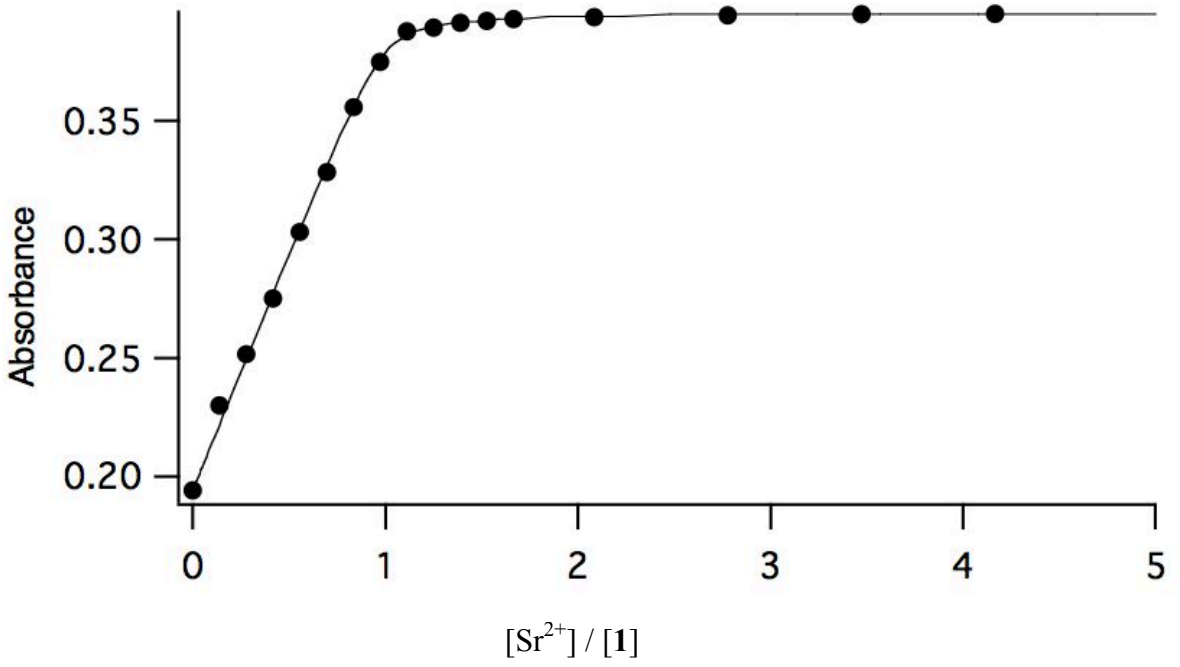



**Figure S20.** (a) Absorbance spectral change of ALDIPY monomer [**1**·$L_2$] (3.5 μM) upon the addition of $Sr(ClO_4)_2$ (0 − 21 μM) in a mixed solvent $CH_3CN/CH_3OH$ = 4:1 (v/v) ($l$ = 1.0 cm, 298 K). (b) The change of absorbance at 604 nm. The solid line represents the calculated 1:1 binding curve ($K_a = 3 \times 10^7$ $M^{-1}$).

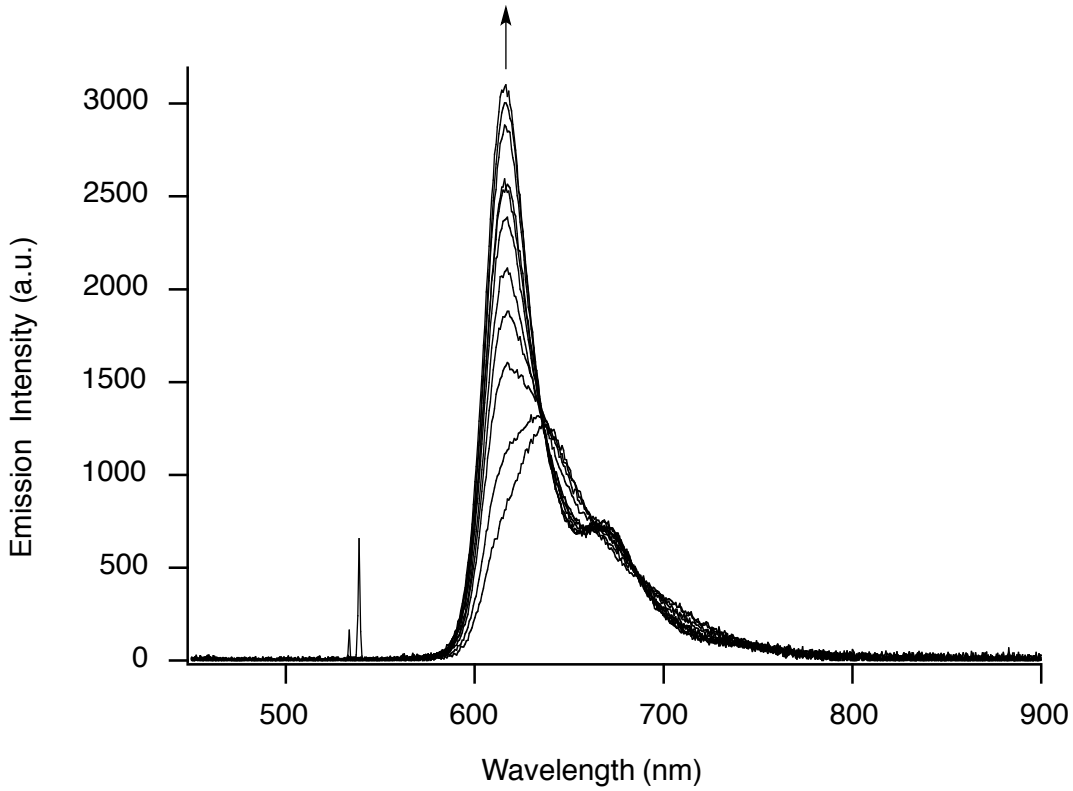
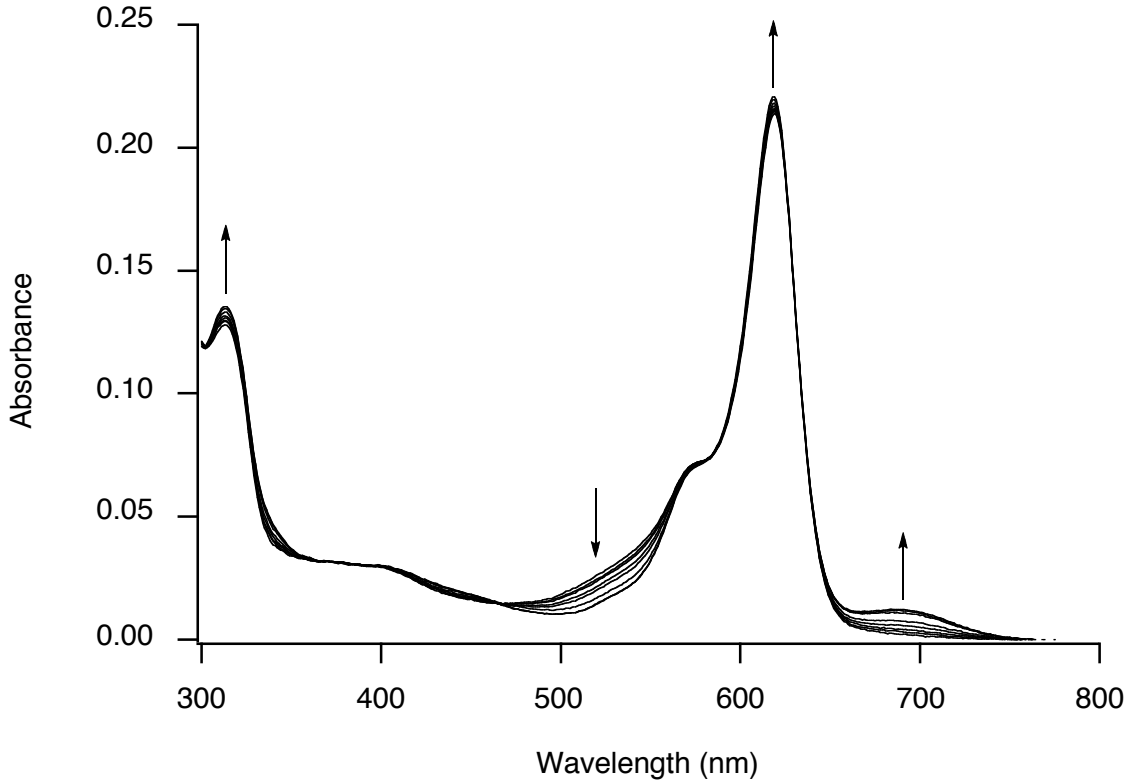



**Figure S21.** Emission spectral changes of ALDIPY monomer [**1**·$L_2$] (5.0 μM) upon the addition of $Ca(ClO_4)_2$ (0 − 37.5 μM) in a mixed solvent $CH_3OH/H_2O$ = 9:1 (v/v) ($\lambda_{ex}$ = 400 nm).

(a)




(b)

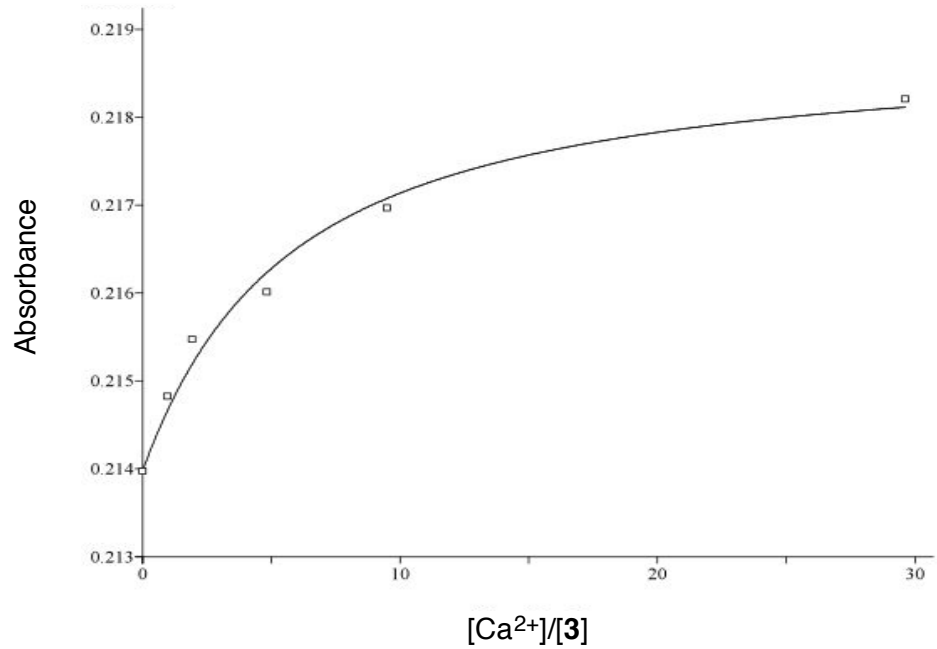
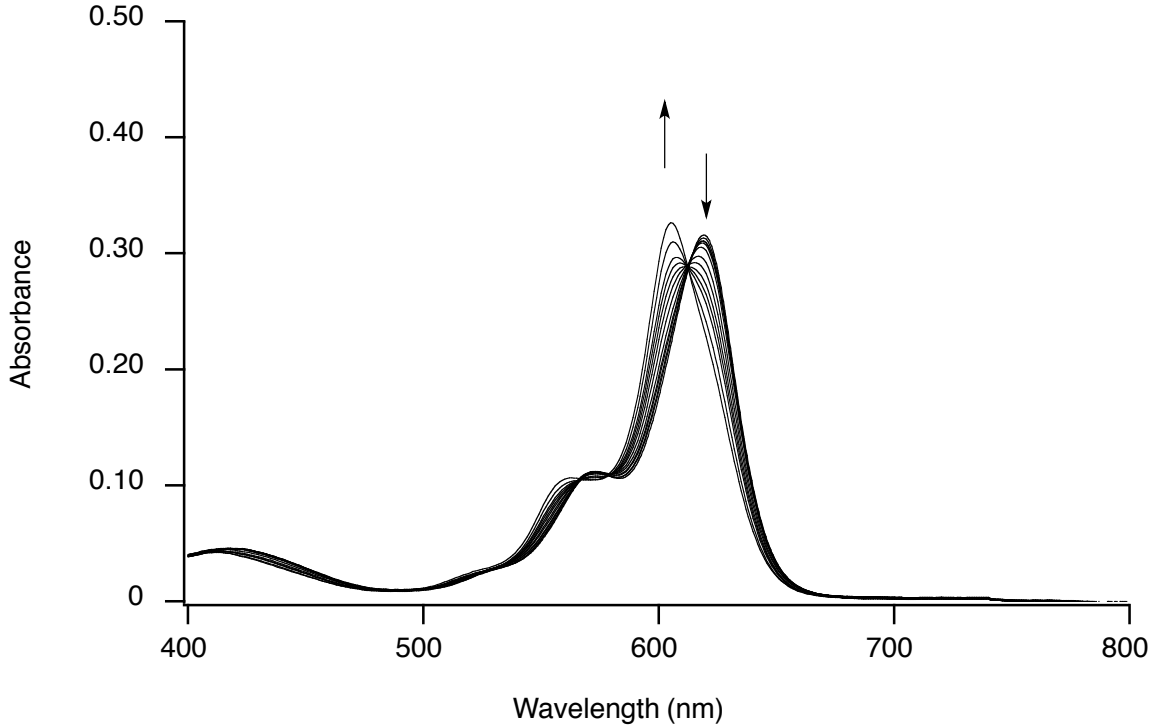



**Figure S22.** (a) Absorbance spectral change of BODIPY monomer **3** (5.0 μM) upon the addition of $Ca(ClO_4)_2$ (0 − 610 μM) in a mixed solvent $CH_3OH/H_2O$ = 9:1 (v/v) ($l$ = 1.0 cm, 298 K). (b) The change of absorbance at 619 nm. The solid line represents the calculated 1:1 binding curve ($K_a = 4.0 \times 10^4$ $M^{-1}$).

(a)




(b)

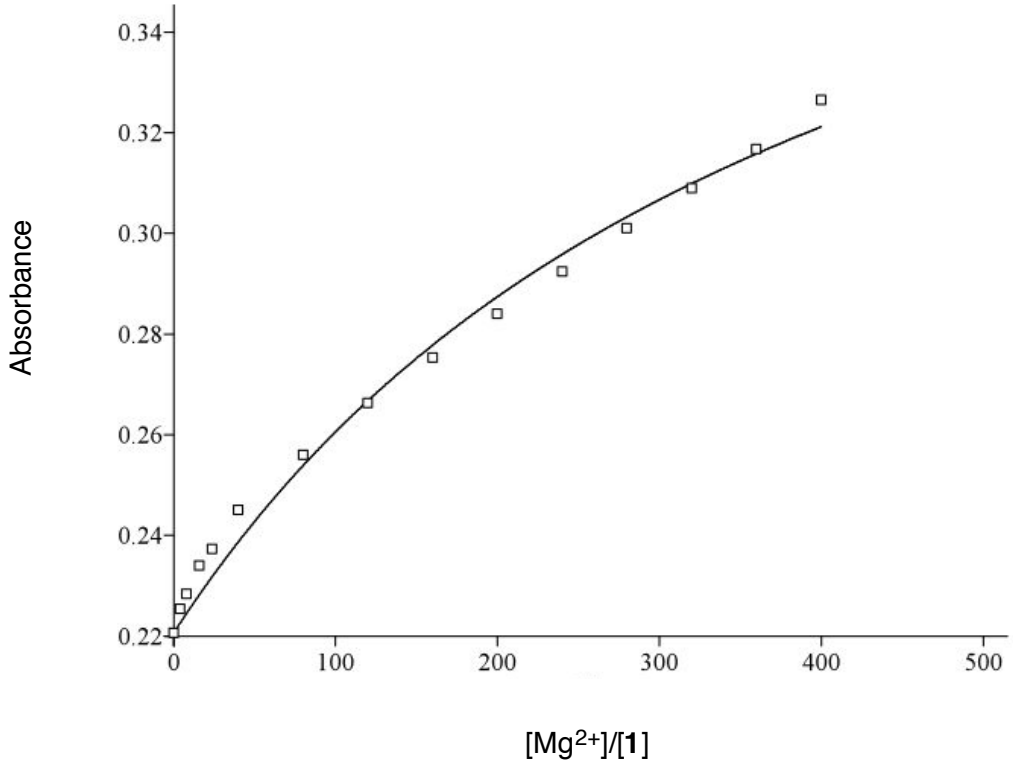
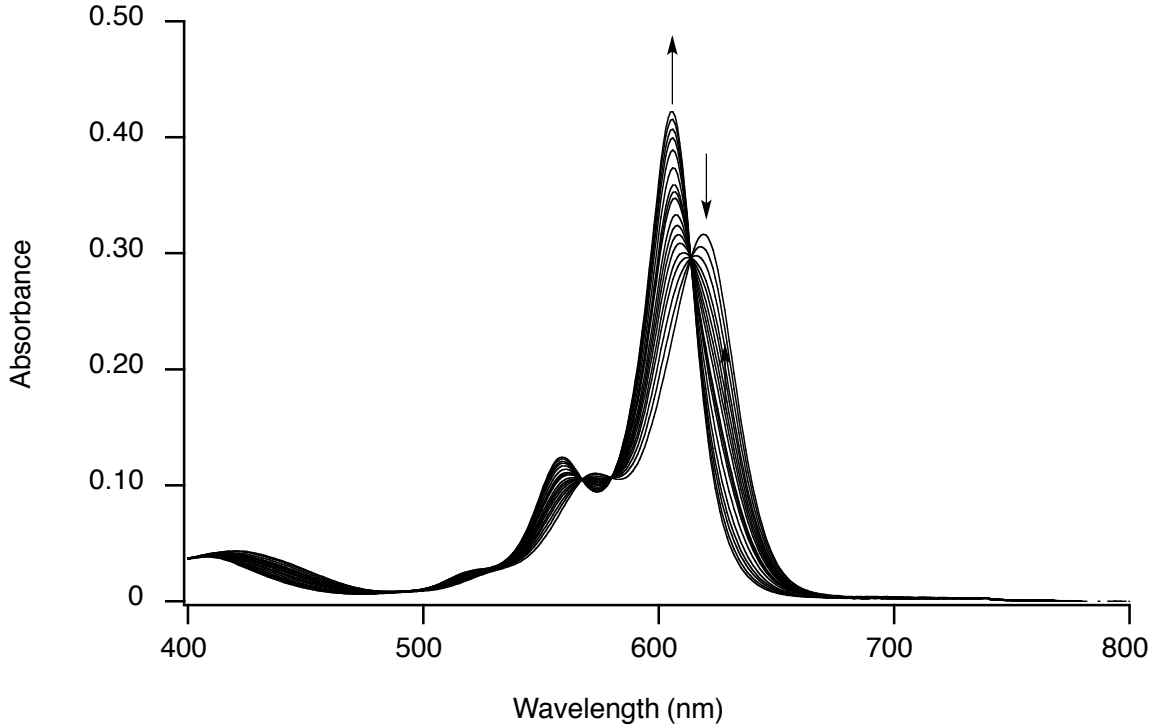



**Figure S23.** (a) Absorbance spectral change of ALDIPY monomer [**1**·$L_2$] (5.0 μM) upon the addition of $Mg(ClO_4)_2$ (0 – 2.0 mM) in a mixed solvent $CH_3OH/H_2O$ = 9:1 (v/v) ($l$ = 1.0 cm, 298 K). (b) The change of absorbance at 605 nm. The solid line represents the calculated 1:1 binding curve ($K_a$ = 490 $M^{-1}$).

(a)




(b)

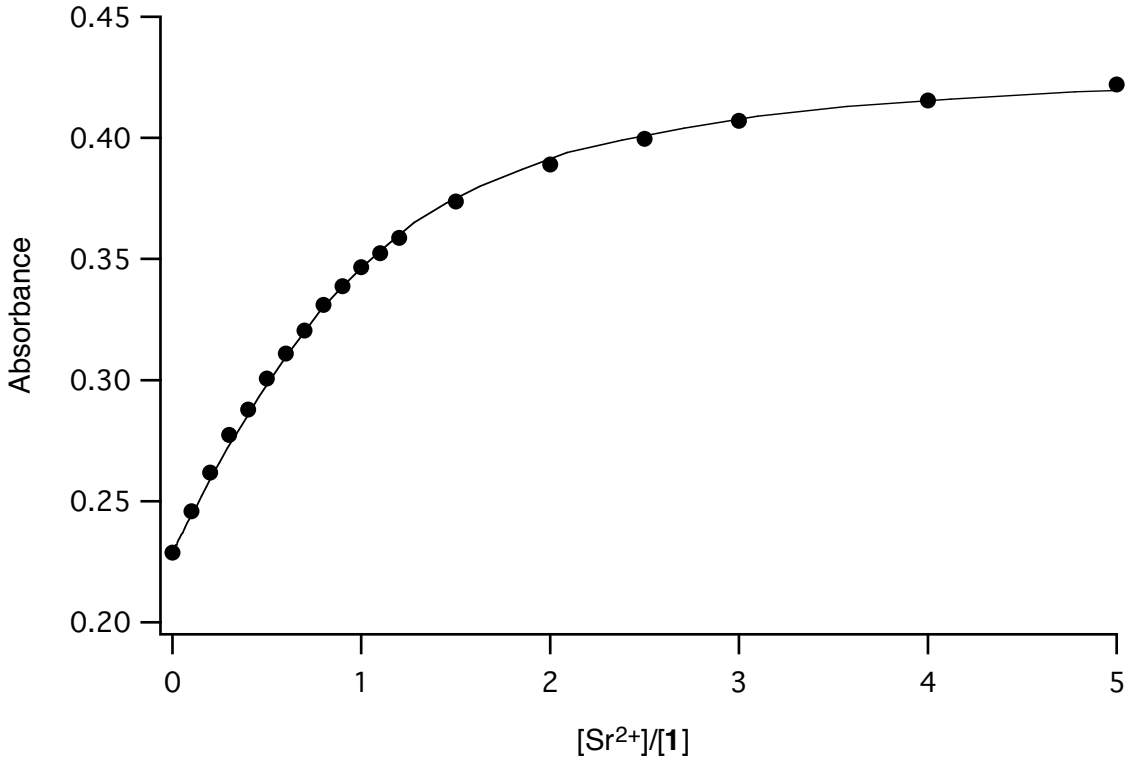
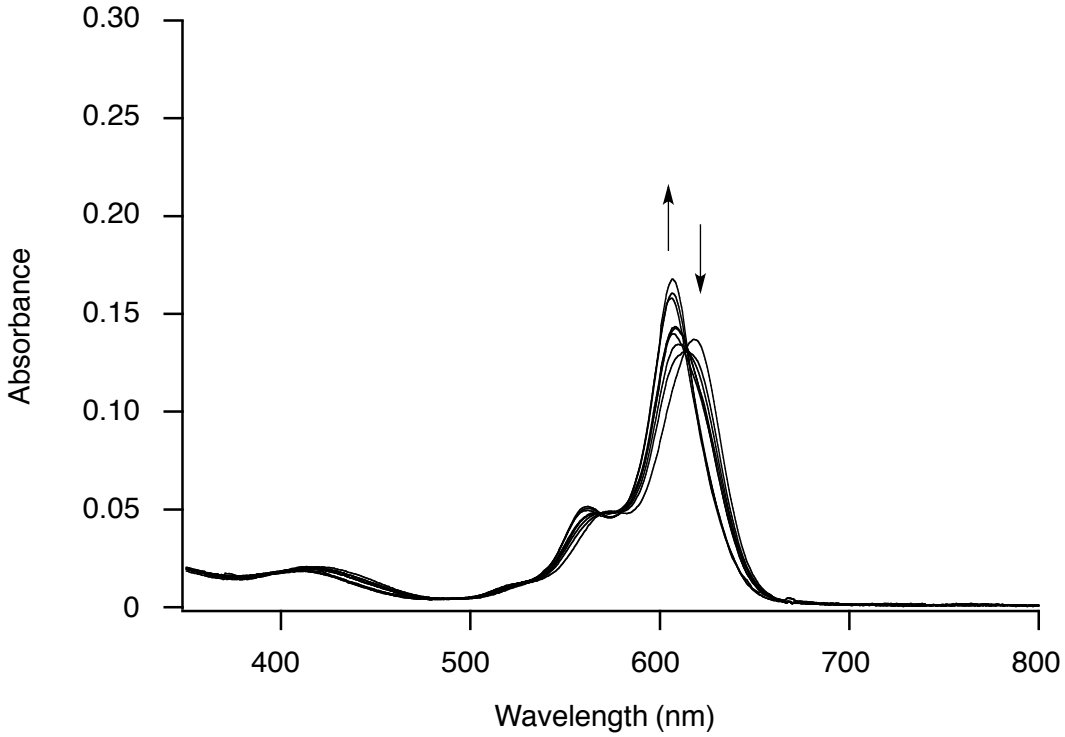



**Figure S24.** (a) Absorbance spectral change of ALDIPY monomer [**1**·$L_2$] (5.0 μM) upon the addition of $Sr(ClO_4)_2$ (0 – 25 μM) in a mixed solvent $CH_3OH/H_2O$ = 9:1 (v/v) ($l$ = 1.0 cm, 298 K). (b) The change of absorbance at 606 nm. The solid line represents the calculated 1:1 binding curve ($K_a = 6.3 \times 10^5$ $M^{-1}$).

(a)




(b)

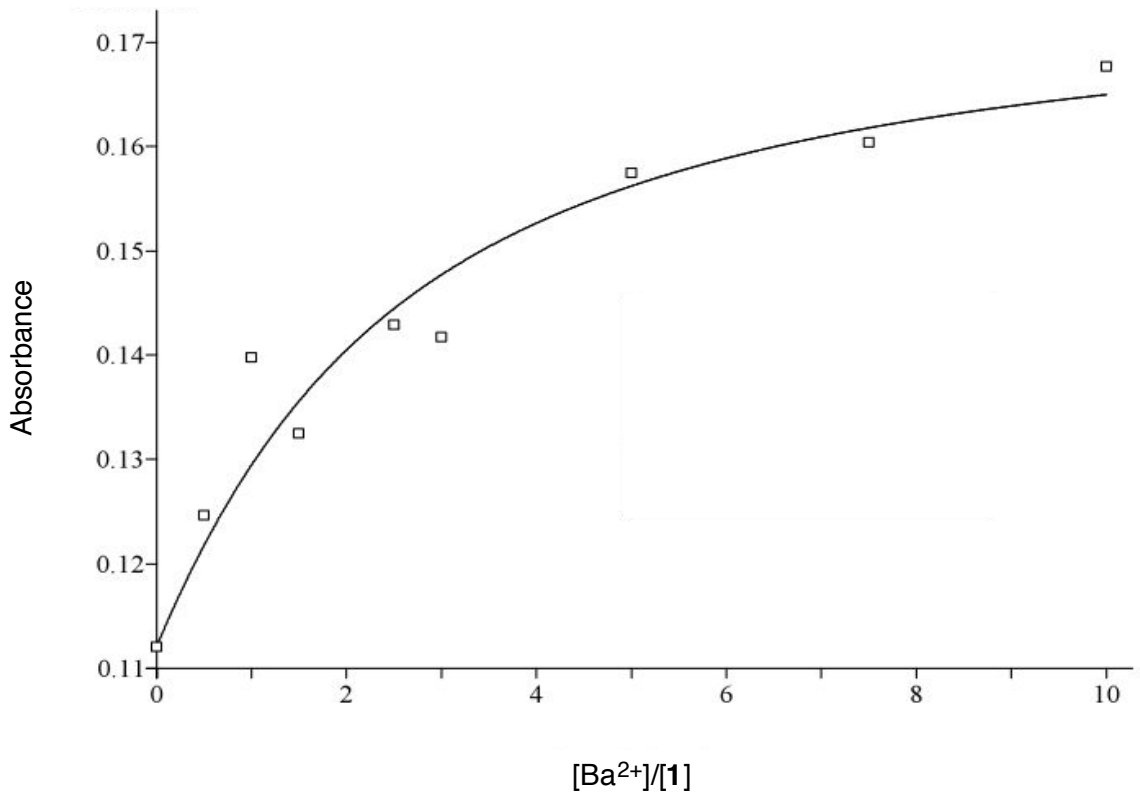
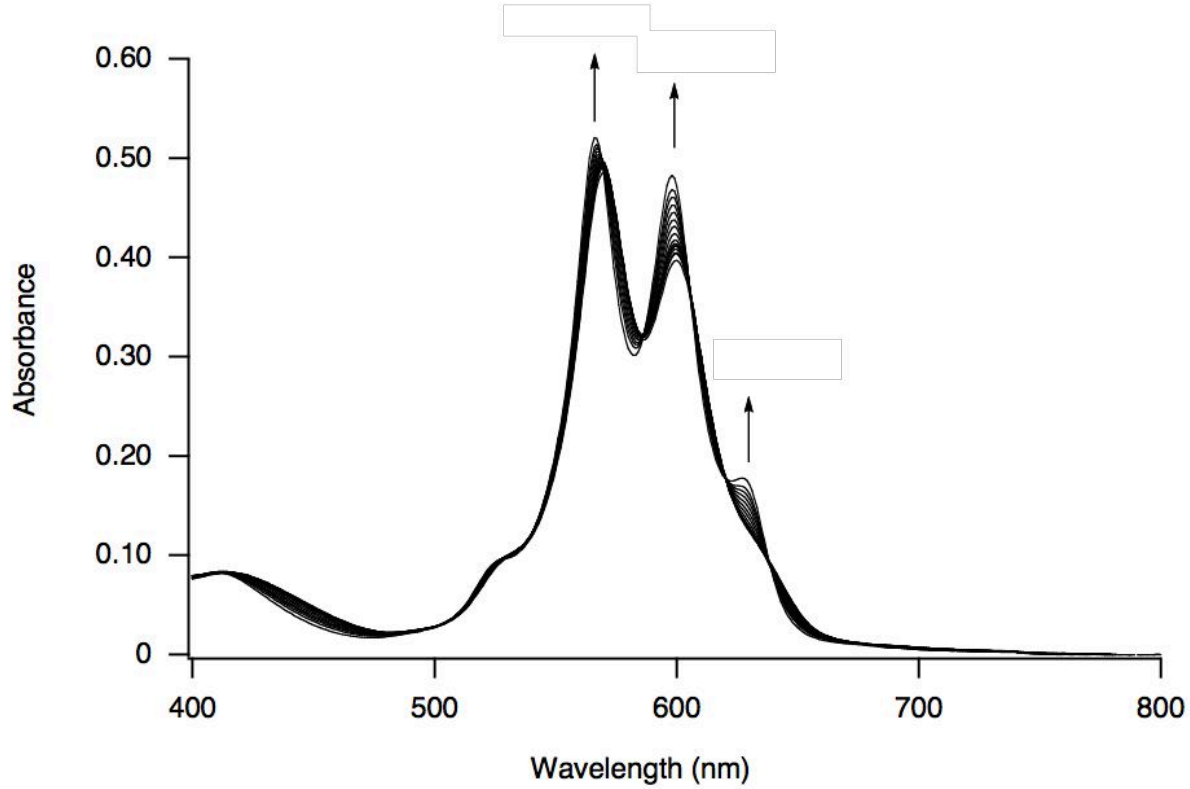



**Figure S25.** (a) Absorbance spectral change of ALDIPY monomer [**1**·$L_2$] (2.5 μM) upon the addition of $Ba(ClO_4)_2$ (0 – 25 μM) in a mixed solvent $CH_3OH/H_2O$ = 9:1 (v/v) ($l$ = 1.0 cm, 298 K). (b) The change of absorbance at 607 nm. The solid line represents the calculated 1:1 binding curve ($K_a = 2.0 \times 10^5$ $M^{-1}$).

**Table S2.** Emission properties of ALDIPY monomer [**1**·$L_2$] (2.5 μM) and its complexes with alkaline earth ions ($CH_3OH/H_2O$ = 9:1, Perchlorate salts, 298 K). Quantum efficiency $\Phi_F$ was measured with 5 eq. (/[**1**]) of each ion.

| Guest | $\lambda_{em}$ [nm] | $\Phi_F$ |
|---|---|---|
| none | 639 | 0.43 |
| $Mg^{2+}$ | 616 | 0.45 |
| $Ca^{2+}$ | 616 | 0.67 |
| $Sr^{2+}$ | 617 | 0.64 |
| $Ba^{2+}$ | 620 | 0.61 |

(a)




(b)

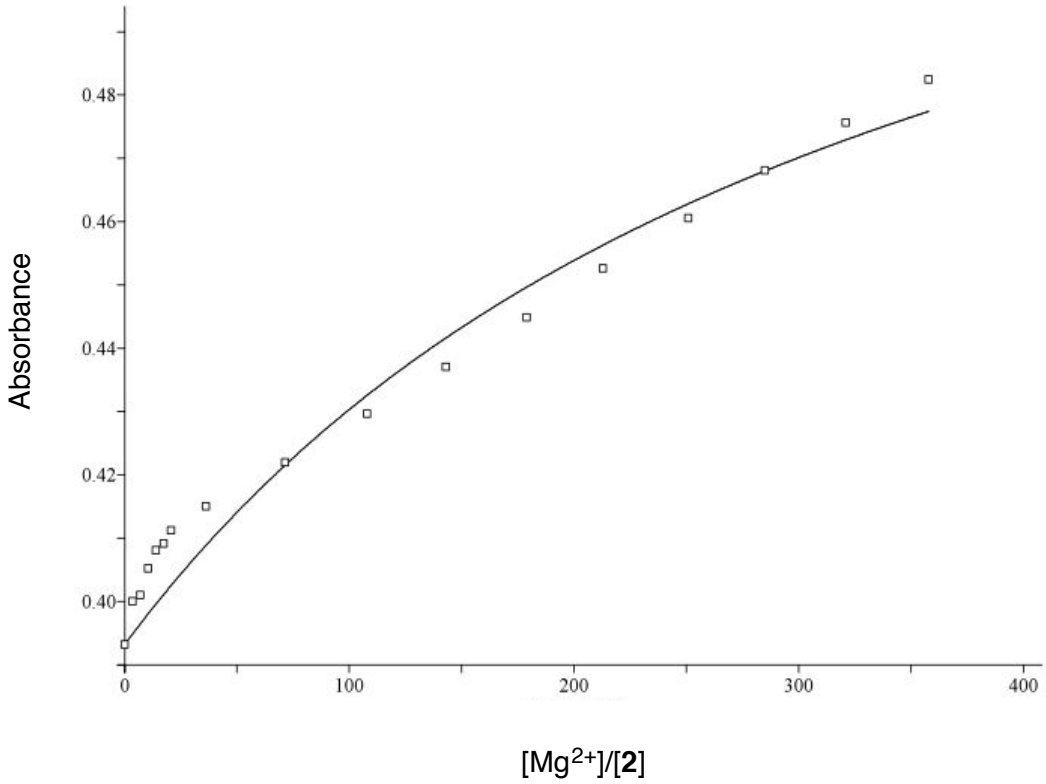
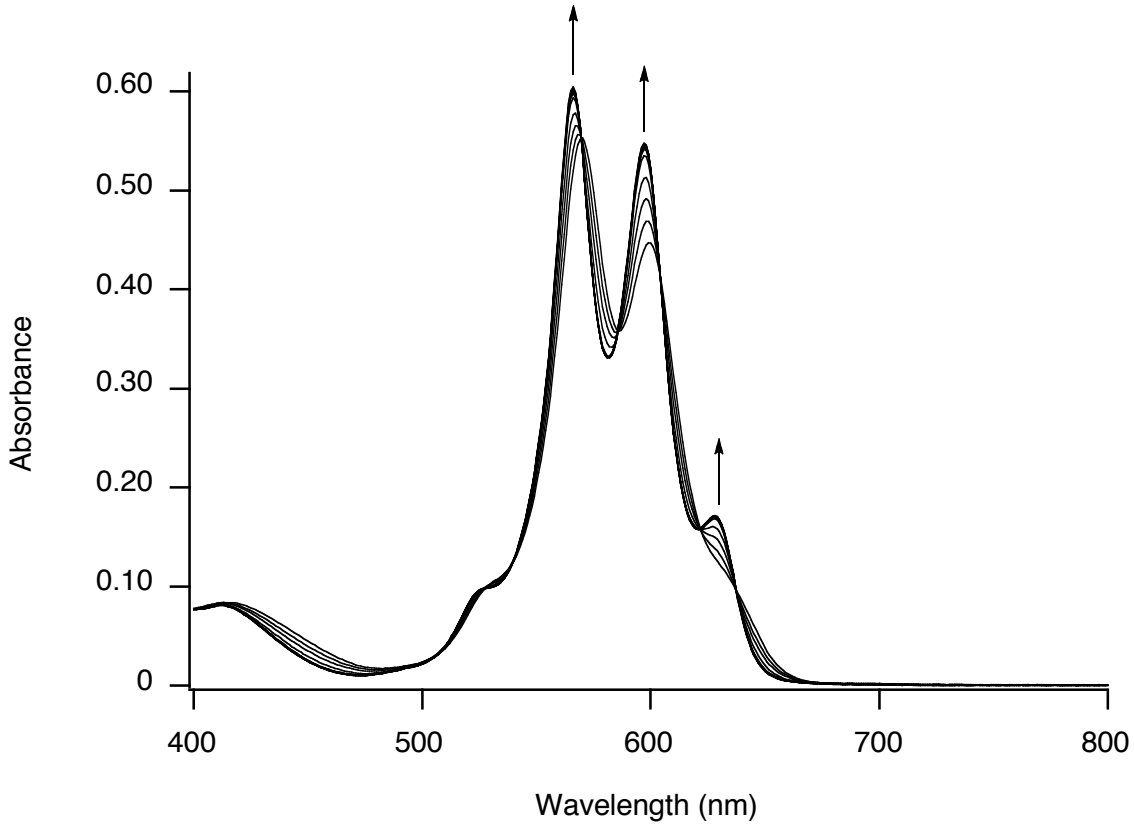



**Figure S26.** (a) Absorbance spectral change of ALDIPY dimer [**2**·$L_4$] (5.0 μM) upon the addition of $Mg(ClO_4)_2$ (0 – 4.0 mM) in a mixed solvent $CH_3OH/H_2O$ = 9:1 (v/v) ($l$ = 1.0 cm, 298 K). (b) The change of absorbance at 598 nm. The solid line represents the calculated 1:1 binding curve ($K_a$ = 580 $M^{-1}$).

(a)




(b)

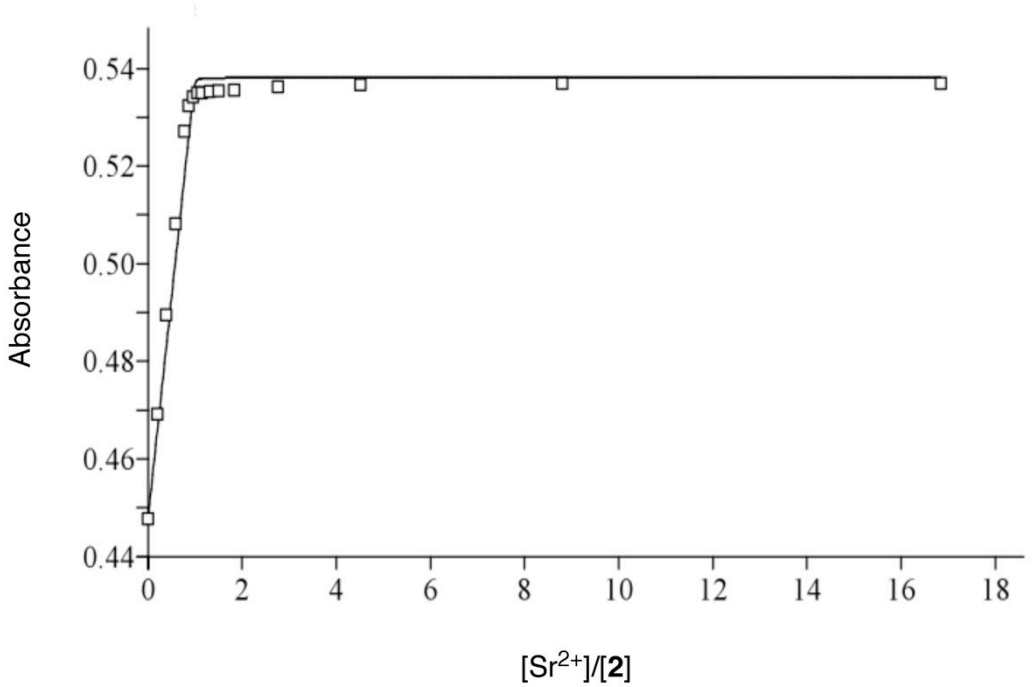
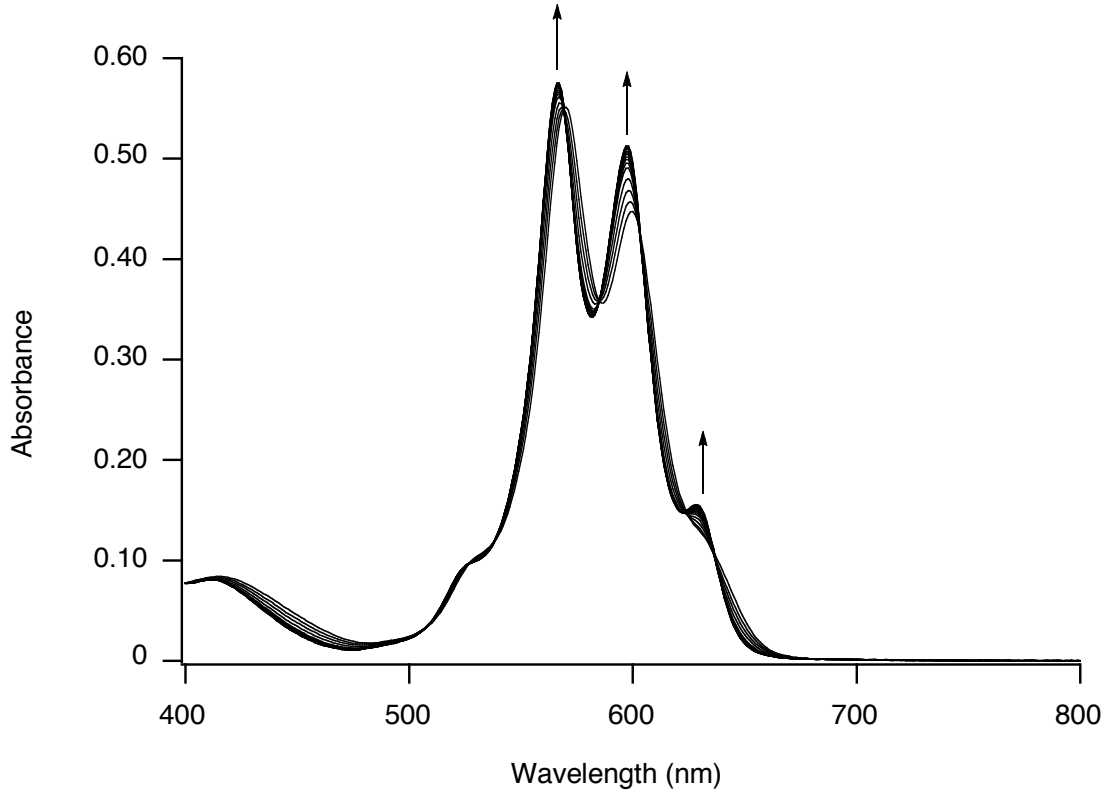



**Figure S27.** (a) Absorbance spectral change of ALDIPY dimer [**2**·$L_4$] (5.0 μM) upon the addition of $Sr(ClO_4)_2$ (0 – 100 μM) in a mixed solvent $CH_3OH/H_2O/CHCl_3$ = 89.5:10:0.5 (v/v/v) ($l$ = 1.0 cm, 298 K). (b) The change of absorbance at 599 nm. The solid line represents the calculated 1:1 binding curve ($K_a = 8 \times 10^8$ $M^{-1}$).

(a)




(b)

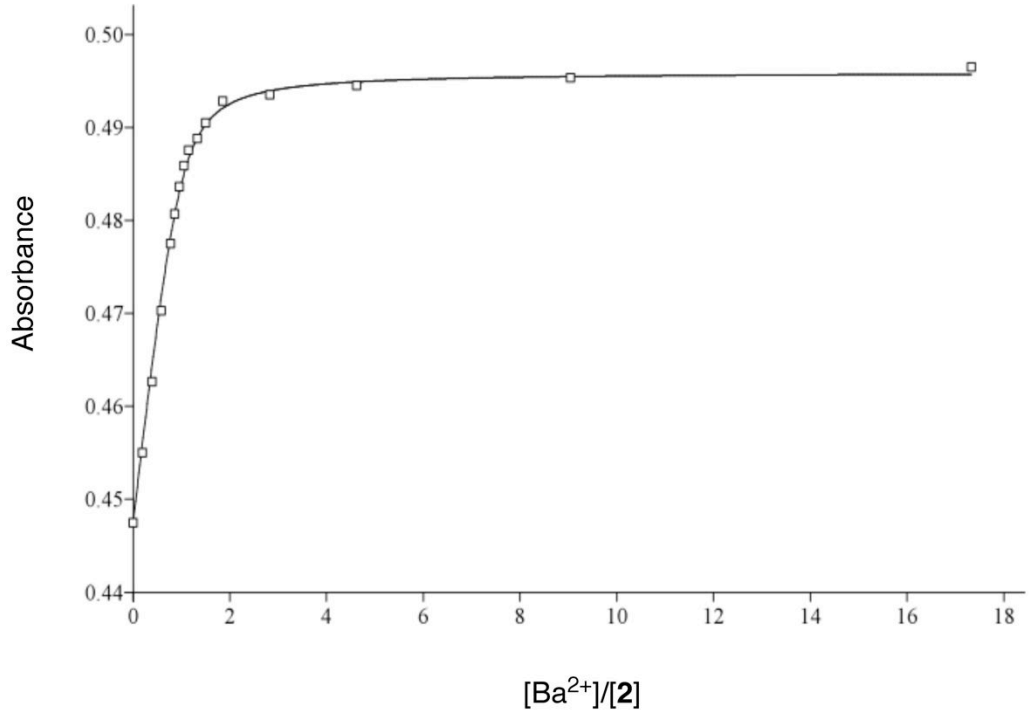



**Figure S28.** (a) Absorbance spectral change of ALDIPY dimer [**2**·$L_4$] (5.0 μM) upon the addition of $Ba(ClO_4)_2$ (0 – 100 μM) in a mixed solvent $CH_3OH/H_2O/CHCl_3$ = 89.5:10:0.5 (v/v/v) ($l$ = 1.0 cm, 298 K). (b) The change of absorbance at 600 nm. The solid line represents the calculated 1:1 binding curve ($K_a = 2.5 \times 10^6$ $M^{-1}$).

**References for the Supporting Information**


1. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176.
2. Bruker, *APEX2*, 2014.
3. (a) K. Wakita, *Yadokari-XG, Software for Crystal Structure Analyses*, 2001; (b) C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *J. Cryst. Soc. Jpn.*, 2009, **51**, 218.
4. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
5. C. Ikeda, N. Sakamoto and T. Nabeshima, *Org. Lett.*, 2008, **10**, 4601.
6. S. Harada, D. Hayashi, I. Sato and M. Hirama, *Synlett*, 2012, **23**, 405.
7. S. Akine, F. Utsuno and T. Nabeshima, *Chem. Commun.*, 2010, **46**, 1029.
8. D. M. Knapp, E. P. Gillis and M. D. Burke, *J. Am. Chem. Soc.*, 2009, **131**, 6961.
9. K. Akine, *Titration*, *ver 1.1.0, For analysis of titration data in host-guest chemistry*, 2013.