The Supporting Information for

Bpytrisalen/bpytrisaloph:
A triangular platform that spatially arranges
different multiple labile coordination sites

Takashi Nakamura, Yuto Kawashima, Eiji Nishibori, Tatsuya Nabeshima*

Graduate School of Pure and Applied Sciences
and Tsukuba Research Center for Energy Materials Science (TREMS),
University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan

*Corresponding Author. E-mail: nabesima@chem.tsukuba.ac.jp
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Materials and methods

Unless otherwise noted, solvents and reagents were purchased from TCI Co., Ltd., FUJIFILM Wako Pure Chemical Co., Kanto Chemical Co., Inc., Nacalai Tesque, Inc., and Sigma-Aldrich Co., and used without further purification. Dry THF and DMF was purified by Glass Contour Ultimate Solvent System 3S-TCN 1. Silica gel for column chromatography was purchased from Kanto Chemical Co. Inc. (Silica Gel 60 N (spherical, 63–210 µm or 40–50 µm)).

Measurements were performed at 298 K unless otherwise noted. ¹H, ¹³C other 2D NMR spectra were recorded on a Bruker AVANCE III-600 (600 MHz) spectrometer or a Bruker AVANCE III-400 (400 MHz) spectrometer. Negative values were depicted in red in the spectra. Tetramethylsilane was used as an internal standard (δ 0.00 ppm) for ¹H and ¹³C NMR measurements. Hexafluorobenzene in CDCl₃ (1 wt %) was used as an external standard (δ −163.0 ppm) for ¹⁹F NMR measurements.

Single-crystal X-ray crystallographic measurements of H₂, [1bZn₆(H₂O)₆(OAc)₄]·2(C₄H₃O)·1.5(C₄H₁₀O), and [1aZn₃Ag₃(H₂O)₁₂(OAc)₂(OTf)₁₂] were performed using a Bruker APEX II ULTRA with MoKα radiation (graphite-monochromated, λ = 0.71073 Å) at 120 K. The collected diffraction images were processed by Bruker APEX2. The initial structure was solved using SHELXS-2013[51] and refined using SHELXL-2016[52], which are running on Yadokari-XG crystallographic software[53].

A single-crystal X-ray crystallographic measurement of [1a·4·Zn₁₂(H₂O)₁₂](OTf)₁₂ was carried out at SPring-8 BL02B1 beamline using a RIGAKU mercury 2 CCD detector. The wavelength of incident X-ray was 0.7 Å and the measurement temperature was controlled at 100K using N₂ gas flow low temperature device. The data were processed by RAPID-AUTO[54] by RIGAKU. The initial structure was solved using SIR2008[55] and refined using SHELXL-2016[52] which are running on WINGX software[56].

CCDC 1884372–1884375 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 a Waters SYNAPT G2 HDMS system or 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. IR spectra were recorded on a JASCO FT/IR-480Plus spectrometer.

Elemental analysis was performed on a Yanaco MT-6 analyzer with tin boats purchased from Elementar. We appreciate Mr. Ikuo Iida and Mr. Masao Sasaki of University of Tsukuba for the measurements.
Synthesis and characterization of bpy linker H$_2$2 and its synthetic intermediates

Scheme S1. Syntheses of 7 and 8

Synthesis of 7$^{[57,58]}$

To a solution of $N,N,N'$-trimethylhexylenedianiline (distilled over Na$_2$CO$_3$ prior to use) (3.0 mL, 23.2 mmol) in 1,2-dimethoxyethane (distilled over MgSO$_4$ prior to use) (18 mL) at −78 °C in a 100 mL two-necked heart-shaped flask, 1.54 M n-BuLi in n-hexane (15.0 mL, 23.2 mmol) was added. The mixture was stirred at −78 °C for 30 min. The mixture was then transferred using a double-tipped needle to a solution of 6$^{[59]}$ (3.60 g, 21.0 mmol) in 1,2-dimethoxyethane (50 mL) at −50 °C. After stirring for 30 min at −50 °C, 1.54 M n-BuLi in n-hexane (20.0 mL, 31.5 mmol) was added and the dark solution was stirred for 2 h at −50 °C. The solution was transferred using a double-tipped needle to a solution of iodine (10.0 g, 39.4 mmol) in 1,2-dimethoxyethane (50 mL) at −72 °C. After stirring at −72 °C for 30 min, the solution was removed from the cooling bath and was allowed to warm for 20 min at room temperature, then quenched with water (50 mL). The mixture was extracted with ether (50 mL × 3) and the combined organic layers were washed with saturated Na$_2$S$_2$O$_3$ aqueous solution (50 mL) and was dried over MgSO$_4$. The mixture was then filtered, evaporated and dried under vacuum to give 4.54 g of crude product (brown solid). Column chromatography (silica gel, CHCl$_3$) was performed to give 3.22 g of a mixture of 6 and 7 (1:3) (lime green solid), which was used for the next step without further purification.

Synthesis of 8

To the mixture of 6 and 7 described above was added $p$-TsOH·H$_2$O (230 mg, 1.21 mmol), and was dissolved in toluene (60 mL). Ethylene glycol (2.0 mL, 36.3 mmol) was added and the mixture was stirred at room temperature for 18 h. The mixture was neutralized with saturated NaHCO$_3$ aqueous solution (100 mL) and was extracted with ether (30 mL × 3). The combined organic layers were dried over MgSO$_4$, filtered, evaporated and dried under vacuum to give 3.46 g of crude product (brown solid). Column chromatography (silica gel, hexane/CHCl$_3$/Et$_3$N = 100:10:1) was performed to give 8 (2.69 g, 7.87 mmol, 37% in 2 steps). Light brown solid; m.p. 99–100 °C;

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.45 (s, 1H), 6.20 (s, 1H), 4.30–4.27 (m, 2H), 4.06–4.03 (m, 2H), 3.96 (s, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$): 161.0, 149.1, 128.0, 119.0, 109.2, 102.4, 77.4, 77.1, 76.8, 65.9, 54.6;

Scheme S2.  Synthesis of 9

Synthesis of 9

8 (2.79 g, 8.96 mmol), 2,4,6-trimethylphenylboronic acid (2.01 g, 12.24 mmol), Pd(PPh₃)₄ (943 mg, 816 µmol), and Cs₂CO₃ (7.98 g, 24.48 mmol) were added into a 200 mL three-necked round-bottomed flask. Under an Ar atmosphere, dry DMF (80 mL) was added and the mixture was stirred at 80 °C for 22 h. The mixture was washed with water (50 mL) and the aqueous layer was extracted with AcOEt (50 mL × 3). The combined organic layers were dried over MgSO₄, filtered, evaporated and dried under vacuum to give 6.14 g of crude product (brown oil). Column chromatography (silica gel hexane/CHCl₃/Et₃N = 500:100:1) was performed to give compound 9 (2.54 g, 7.61 mmol, 93%). Light brown solid, m.p. 119–120 °C;

¹H NMR (400 MHz, CDCl₃): δ 6.89 (s, 2H), 6.63 (s, 1H), 5.67 (s, 1H), 4.03 (s, 3H), 3.80–3.75 (m, 4H), 2.31 (s, 3H), 1.98 (s, 6H);

¹³C NMR (101 MHz, CDCl₃): δ 161.5, 153.8, 147.8, 136.4, 134.2, 132.9, 126.8, 116.7, 115.6, 99.0, 64.8, 53.4, 20.0, 19.4;

Elemental analysis: Calcd for C₁₈H₂₀₂N₁O₃.₁ (9·0.1H₂O): C, 64.42; H, 6.07; N, 4.17.  Found C, 64.14; H, 5.90; N, 4.14.
Synthesis of 10

9 (2.79 g, 8.36 mmol) and 2,2'-bipyridine (907 mg, 8.38 mmol) were added into a 100 mL Schlenk tube. Ni(cod)$_2$ (2.61 g, 9.49 mmol) was weighed in a glove box and was added to the flask under an N$_2$ atmosphere. 1,5-COD (1.9 mL, 10.87 mmol) and dry DMF (25 mL) was added, and the reaction mixture was stirred at room temperature for 22 h. After transferring the reaction mixture to a 300 mL pear-shaped flask, the remaining 1,5-COD and DMF were evaporated under reduced pressure, and to the residue was added in CHCl$_3$ (100 mL). A solution of NaOH (1.50 g, 37.50 mmol) and EDTA•2Na•2H$_2$O (6.85 g, 18.40 mmol) in water (100 mL) was added and was stirred under an ambient condition for 2 h. After being stirred for 2 h, the mixture separated into two layers (aqueous layer: blue solution, organic layer: grey suspension). The organic layer was separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (50 mL × 3). The combined organic layers were dried over MgSO$_4$, filtered, evaporated and dried under vacuum to give 3.45 g of crude product (light brown solid). The crude product was washed with hexane to give 10 (2.13 g, 3.57 mmol, 86%).

Light brown solid, m.p. >300 °C

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.76 (s, 2H), 6.94 (s, 4H), 5.74 (s, 2H), 4.02 (s, 6H), 3.84–3.77 (m, 8H), 2.35 (s, 6H), 2.04 (s, 12H);

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 162.2, 153.3, 152.8, 137.0, 135.8, 135.6, 127.8, 118.1, 115.6, 100.6, 65.9, 53.8, 21.1, 20.6;

Elemental analysis: Calcd for C$_{36}$H$_{42}$N$_2$O$_7$ (10•H$_2$O): C, 70.34; H, 6.89; N, 4.56. Found C, 70.24; H, 6.61; N, 4.55.
**Scheme S4.** Synthesis of 11

![Diagram of Scheme S4]

Synthesis of **11**

**10** (609 mg, 1.02 mmol), dry THF (50 mL), 1 M HCl aqueous solution (10 mL) was added into a 200 mL pear-shaped flask and was refluxed under an open atmosphere for 1 h. The mixture was neutralized with saturated NaHCO₃ aqueous solution (20 mL) and was extracted with CH₂Cl₂ (50 mL × 3). The combined organic layers were dried over MgSO₄, filtered, evaporated and dried under vacuum to give **11** (506 mg, 995 µmol, 97%); Yellow solid, m.p. >300 °C

¹¹H NMR (400 MHz, CDCl₃): δ 10.04 (s, 2H), 7.95 (s, 2H), 6.99 (s, 4H), 4.14 (s, 6H), 2.37 (s, 6H), 2.01 (s, 12H);

¹³C NMR (101 MHz, CDCl₃): δ 189.5, 163.5, 156.4, 155.9, 137.9, 134.7, 134.0, 128.4, 117.7, 117.4, 54.4, 21.1, 20.5;

Elemental analysis: Calcd for C₃₂H₃₂.8N₂O₄.4 (11·0.4H₂O): C, 74.51; H, 6.41; N, 5.43. Found C, 74.61; H, 6.45; N, 5.36.
Scheme S5. Synthesis of H$_2$2

$$\begin{array}{c}
\text{O-} & \text{N} & \text{N-} & \text{O-} \\
\text{MeO} & & & \text{MeO}
\end{array} \xrightarrow{\text{BBr}_3} \begin{array}{c}
\text{O-} & \text{N} & \text{N-} & \text{O-} \\
\text{HO} & & & \text{HO}
\end{array}$$

Synthesis of H$_2$2

\textbf{11} (207 mg, 407 µmol) was added into a 100 mL three-necked round-bottomed flask. Under an Ar atmosphere, dry CH$_2$Cl$_2$ (40 mL) and BBr$_3$ (400 µL, 4.3 mmol) was added and the reaction mixture was stirred at room temperature for 1 h. The mixture was quenched with methanol (10 mL) and was evaporated to give 381 mg of crude product (brown solid). The crude product was then dissolved in CHCl$_3$ and was washed with water and brine. The organic layer was dried over Na$_2$SO$_4$, filtered, and evaporated to give to give H$_2$2 (191 mg, 397 µmol, 97%).

Orange solid, m.p. $>$300 °C

$^1$H NMR (600 MHz, CDCl$_3$, 225 K): $\delta$ 12.41 (s, 1H), 12.26 (s, 1H), 11.07 (s, 2H), 9.97 (s, 2H), 9.62 (s, 1H), 9.60 (s, 1H), 8.20 (s, 1H), 7.34 (s, 1H), 7.00 (s, 2H), 6.99 (s, 2H), 6.95 (s, 4H), 6.72 (s, 2H), 2.38 (s, 6H), 2.35 (s, 3H), 2.33 (s, 3H), 2.06 (s, 12H), 2.02 (s, 6H), 2.01 (s, 6H);

$^{13}$C NMR (151 MHz, CDCl$_3$, 225 K): $\delta$ 195.5, 195.2, 189.8, 165.2, 165.1, 161.3, 160.1, 159.1, 158.7, 158.4, 151.0, 144.0, 139.3, 138.6, 138.3, 135.0, 134.9, 133.6, 132.5, 130.4, 129.5, 128.6, 128.3, 123.9, 117.3, 115.5, 113.9, 113.7, 108.0, 21.2, 20.8, 20.7, 20.4.;

HRMS (ESI): observed m/z 481.2099 ([M+H]$^+$). calcd. 481.2127.

IR (KBr): 3446 (br), 3094 (m), 2951 (m), 2920 (m), 2862 (m), 1694 (s), 1654 (s), 1625 (s), 1572 (s) 1540 (m), 1521 (s), 1460 (s), 1375 (m), 1303 (w), 1266 (w), 1237 (w), 1207 (w), 1169 (w), 1117 (w), 1081 (w), 1033 (w), 961 (w), 923 (w), 897 (w), 851 (m), 808 (w), 791 (w), 745 (w), 730 (w), 681 (w), 627 (w), 580 (m), 557 (m) cm$^{-1}$. 

S8 / S56
Characterization data

Figure S1. \textsuperscript{1}H NMR spectrum of 8 (CDCl\textsubscript{3}, 400 MHz).

Figure S2. \textsuperscript{13}C NMR spectrum of 8 (CDCl\textsubscript{3}, 101 MHz).
Figure S3. $^1$H NMR spectrum of 9 (CDCl$_3$, 400 MHz).

Figure S4. $^{13}$C NMR spectrum of 9 (CDCl$_3$, 101 MHz).
Figure S5. $^1$H NMR spectrum of 10 (CDCl$_3$, 400 MHz).

Figure S6. $^{13}$C NMR spectrum of 10 (CDCl$_3$, 101 MHz).
Figure S7. $^1$H NMR spectrum of 11 (CDCl$_3$, 400 MHz).

Figure S8. $^{13}$C NMR spectrum of 11 (CDCl$_3$, 101 MHz).
Figure S9. $^1$H NMR of H$_2$2 (CDCl$_3$, 600 MHz, 225 K).

Figure S10. $^{13}$C NMR of H$_2$2 (CDCl$_3$, 151 MHz, 225 K).
Figure S10. (continued) $^{13}$C NMR of H$_2$2 (CDCl$_3$, 151 MHz, 225 K).
Figure S11. $^1$H–$^{13}$C HSQC spectrum of H$_2$2 (CDCl$_3$, 600 MHz, 225 K).

Figure S12. $^1$H–$^{13}$C HMBC spectrum of H$_2$2 (CDCl$_3$, 600 MHz, 225 K).
Figure S13. IR spectrum of H$_2$ (KBr).

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A single crystal of H$_2$2 suitable for an X-ray diffraction analysis was obtained by the slow diffusion of hexane vapor into a chloroform solution of H$_2$2. Solvent accessible voids of 482 cubic angstroms (30% of the cell volume) were found. Due to the heavy disorder of the solvent molecules (chloroform and hexane), their positions were not determined.

Crystal data for H$_2$2: C$_{30}$H$_{28}$N$_2$O$_4$, $F_w = 480.54$, yellow block, $0.15 \times 0.09 \times 0.08$ mm$^3$, monoclinic, space group $P 2_1/c$ (No. 14), $a = 7.146(2)$ Å, $b = 8.659(3)$ Å, $c = 25.637(8)$ Å, $\beta = 92.646(3)^\circ$, $V = 1584.6(9)$ Å$^3$, $Z = 2$, $R_1 = 0.1240$, $wR_2 = 0.3722$, GOF = 2.395. CCDC 1884372.

**Figure S14.** The molecular structure of H$_2$2 determined by X-ray diffraction analysis. C, light green; N, blue; O, red; H, white. (a–c) An ellipsoidal model (50% probability). Hydrogen atoms were omitted for clarity. (a) Top view. (b) Side view. (c) Intermolecular hydrogen bonds. (d) Crystal packing viewed along $a$ axis. Space-filling model.
Synthesis and characterization of macrocyclic ligands and their complexes

Scheme S6. Synthesis of H$_6$1a

Synthesis of H$_6$1a

H$_2$2 (780 mg, 1.62 mmol), (1R,2R)-(–)-cyclohexanediamine (186 mg, 1.62 µmol), and CHCl$_3$ (30 mL) were added to a 50 mL pear-shaped flask. The yellow solution was stirred at 60 °C for 1 h. The solvent was evaporated and the residue was dissolved again in 2 mL of CHCl$_3$. Hexane was added by vapor diffusion to give brown oily solids in a yellow solution. The solid was separated by decantation and the yellow solution was evaporated to give H$_6$1·7H$_2$O (388 mg, 646 µmol, 85%).

Yellow solid, m.p. decomposed at 190 °C

$^1$H NMR (600 MHz, CDCl$_3$): δ 14.05 (s, 6H), 7.85 (s, 6H), 7.80 (s, 6H), 7.00 (s, 6H), 6.94 (s, 6H), 3.20–3.18 (m, 6H), 2.36 (s, 18H), 1.94 (s, 18H), 1.77 (br, 6H), 1.72 (br, 6H), 1.64 (s, 18H), 1.61 (br, 6H), 1.34 (br, 6H);

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 165.4, 161.0, 156.0, 154.3, 137.8, 135.8, 135.1, 132.9, 128.5, 128.0, 115.4, 111.8, 73.5, 32.8, 24.0, 21.1, 20.5, 20.1;

UV (CHCl$_3$): $\lambda_{\text{max}}$ 360 nm ($\varepsilon = 1.14 \times 10^5$ [M$^{-1}$·cm$^{-1}$]);

FL (CHCl$_3$): $\lambda_{\text{max}}$ 495 nm ($\lambda_{\text{ex}}$ = 360 nm);

Emission quantum yield: $\Phi_F = 0.16$ ($\lambda_{\text{ex}}$ = 360 nm);

HRMS (ESI): observed m/z 559.6414 ([M+H$_3$]$^{+}$), calcld. 559.6417.

Elemental analysis: Calcd for C$_{108}$H$_{128}$N$_{12}$O$_{13}$ (H$_6$1a·7H$_2$O): C, 71.97; H, 7.16; N, 9.33. Found C, 72.10; H, 7.10; N, 9.33.

IR (KBr): 3436 (br), 3339 (br), 2927 (s), 2859 (s), 2736 (m), 1620 (s), 1583 (s), 1536 (s), 1506 (s), 1449 (s), 1377 (s), 1314 (m), 1295 (m), 1269 (m), 1242 (w), 1219 (m), 1173 (w), 1146 (m), 1089 (m), 1062 (w), 1038 (m), 985 (w), 961 (w), 929 (m), 850 (s), 822 (s), 795 (w), 754 (m), 680 (w), 665 (w), 633 (m), 590 (w), 553 (w), 529 (w) cm$^{-1}$. 

S18 / S56
Scheme S7. Synthesis of 1aZn₆(H₂O)₁₁(OAc)₆

Synthesis of 1aZn₆(H₂O)₁₁(OAc)₆

H₆1•7H₂O (16.8 mg, 9.32 µmol), Zn(OAc)₂·2H₂O (22.0 mg, 100 µmol), CHCl₃ (4 mL), and MeOH (4 mL) were added to a 20 mL Schlenk tube. The solution was stirred at room temperature for 30 min. The solvent was washed with water and the organic layer was evaporated and was dissolved again in 500 µL of THF. After filtering the THF solution, n-pentane was added by vapor diffusion which gave red solids in a red solution. The precipitated solids were collected by filtration to give 1aZn₆(H₂O)₁₁(OAc)₆ (22.0 mg, 8.41 µmol, 90%).

Red powder, m.p. decomposed at 155 °C

1H NMR (600 MHz, CDCl₃): δ 7.91 (s, 6H), 6.97 (s, 6H), 6.92 (s, 12H), 6.25 (br), 3.90 (br), 2.98 (br, 6H), 2.32 (s, 18H), 2.03–2.00 (m, 54H), 1.77–1.76 (m, 12H), 1.22 (br, 6H), 0.99 (br, 6H);

13C NMR (151 MHz, CDCl₃): δ 178.5, 168.6, 158.6, 150.7, 138.1, 135.0, 133.6, 128.4, 116.6, 109.9, 65.4, 27.5, 23.9, 23.2, 21.1, 20.7, 20.4;

UV (CHCl₃): λ_max 418 nm (ε = 1.16 × 10⁵ [M⁻¹·cm⁻¹]);

FL (CHCl₃) λ_max 470 nm (λ_ex = 420 nm);

Emission quantum yield: Φₑ = 0.12 (λ_ex = 420 nm);

ESI-MS: observed m/z 718.47 ([1aZn₁₆(CH₃O)₃])⁺. calcd. 718.49.

Elemental analysis: Calcd for C₁₂₀H₁₄₈N₁₂O₂₉Zn₁₆ (1aZn₁₆(H₂O)₁₁(OAc)₆): C, 55.12; H, 5.71; N, 6.43. Found: C, 55.26; H, 5.52; N, 6.53.
**Scheme S8.** Synthesis of 1bZn₆(H₂O)₈(OAc)₆

\[ \text{H}_2\text{2} (24.5 \text{ mg}, 50 \mu\text{mol}), 1,2\text{-phenylenediamine (5.5 mg, 50 \mu mol), Zn(OAc)₂·2H₂O (14.5 mg, 65 \mu mol), CHCl₃ (1 mL), and MeOH (1 mL) were added to a 20 mL Schlenk tube. The solution was stirred at 60 °C for 20 h. The solvent was evaporated and the remaining red solids were dissolved again in 1 mL of CHCl₃. After filtering the CHCl₃ solution, } \text{n-pentane was added by vapor diffusion which gave red solids in a red solution. The precipitated solids were filtered and washed with hexane to give 1bZn₆(H₂O)₈(OAc)₆ (8.2 mg, 3.2 \mu mol, 30\%). Red powder, m.p. decomposed at 150 °C.} \]

\[ ^1\text{H NMR (400 MHz, CDCl₃):} \delta 8.44 (s, 6H), 7.19–7.17 (m, 6H), 7.07 (s, 6H), 6.99 (s, 12H), 6.89–6.87 (m, 6H), 2.37 (s, 18H), 2.07 (br, 54H). \]

Elemental analysis: Calcd for C₁₂₀H₁₂₄N₁₂O₂₈Zn₆ (1bZn₆(H₂O)₈(OAc)₆): C, 56.69; H, 4.92; N, 6.61. Found: C, 56.69; H, 4.89; N, 7.00.
Synthesis of 1aZn_{6}(H_{2}O)_{22}(OTf)_{6}

H_{6}1a•7H_{2}O (150.4 mg, 83.47 µmol), and CHCl_{3} (5 mL) were added to a 30 mL pear-shaped flask. Zn(OAc)_{2}•2H_{2}O (250 µmol) in MeOH (925 µL) and Zn(OTf)_{2} (266 µmol) in MeOH (875 µL) were added and the yellow solution was stirred at room temperature for 1 h. After the solvent was evaporated, the crude product was repeatedly dissolved in CHCl_{3} (2 mL) and MeOH (4 mL) and evaporated to remove the volatile AcOH. After repeating the dissolution-evaporation procedure five times, the product was dried under reduced pressure to give 1aZn_{6}(H_{2}O)_{22}(OTf)_{6} (267 mg, 79.3 µmol, 95%). The amount of H_{2}O was determined from the 1H NMR measurement. Yellow solids, m.p. >300 °C

1H NMR (600 MHz, CDCl_{3}): δ 7.99 (s, 6H), 7.13 (s, 6H), 6.95 (s, 12H), 3.36 (br, 6H), 2.33 (s, 18H), 2.24 (s, 18H), 2.02 (s, 18H), 1.81 (br, 12H), 1.24 (br, 6H), 1.00 (br, 6H);

13C NMR (151 MHz, CDCl_{3}): δ 168.2, 160.6, 149.7, 138.5, 135.5, 134.9, 132.9, 128.6, 128 5, 120.8, 118.7, 116.7, 111.5, 65.1, 27.1, 23.6, 21.1, 20.3, 20.1;

19F NMR (565 MHz, CDCl_{3}): δ –78.4.

UV (CHCl_{3}): λ_{max} 411 nm (ε = 1.2 × 10^{5} [M^{-1}·cm^{-1}]);
FL (CHCl_{3}) λ_{max} 463, 487 nm (λ_{ex} = 413 nm);
Emission quantum yield: Φ_{F} = 0.43 (λ_{ex} = 410 nm);
ESI-MS: observed m/z 718.47 ([1aZna(CH_{3}O)_{3}]^{3+}). calcd. 718.49.
Scheme S10. Synthesis of 1aZn₃Ag₃(H₂O)₁₁(AcOH)₂(TfO)₃

To a 20 mL pear shaped flask, H₆1a (37.3 mg, 20.7 µmol), CHCl₃ (2.5 mL) and CH₃CN (2.5 mL) was added. To the mixture, AgOTf (62.2 µmol) was added as a CHCl₃/CH₃CN = 1 : 1 solution and the solution was stirred at room temperature for 5 minutes. Next, Zn(OAc)₂•2H₂O (62.2 µmol) was added as a CHCl₃/CH₃OH = 1 : 1 solution and the solution was stirred at room temperature for 5 minutes. The solvent was evaporated under reduced pressure to give a yellow solid. The solid was dissolved in CHCl₃ (2.5 mL)/CH₃CN (2.5 mL) and the solvent was evaporated again. This dissolution and evaporation procedure was conducted three times in order to remove volatile AcOH. The obtained yellow solid was dissolved in CHCl₃ (1.5 ml) and cyclohexane was added by vapor diffusion. Small crystals appeared after 3 day at room temperature. The crystals were filtered and dried under reduced pressure to give 1aZn₃Ag₃(H₂O)₁₁(AcOH)₂(TfO)₃ (23.6 mg, 8.2 µmol, 40%).

Yellow crystals; m.p. decomposed at 250 °C

¹H NMR (600 MHz, CDCl₃): δ 7.99 (s, 6H), 7.12 (s, 6H), 6.95 (s, 12H), 2.34 (br, 6H), 2.07 (s, 24H), 2.07 (s, 18H), 2.03 (s, 18H), 1.80 (br, 12H), 1.24 (br, 6H), 1.00 (s, 6H).

¹⁹F NMR (565 MHz, CDCl₃): δ −78.1.

UV (CHCl₃): λmax 411 nm (ε = 1.0 × 10⁵ [M⁻¹·cm⁻¹]);

FL (CHCl₃) λmax 462, 488 nm (λex = 411 nm);

Emission quantum yield: Φₑ = 0.16 (λex = 411 nm);

ESI-MS: observed m/z 1112.2 ([1aZn₃Ag₃(H₂O)(OH)]²⁺). calcd. 1112.1.

Elemental analysis: Calcd for C₁₁₅H₁₃₈F₅₀N₁₂O₁₀S₃Zn₃ (1aZn₃Ag₃(H₂O)₁₁(AcOH)₂(TfO)₃): C, 46.74; H, 4.71; N, 5.69. Found C, 46.62; H, 4.43; N, 5.54.
Figure S15. $^1$H NMR of H$_6$1a (CDCl$_3$, 600 MHz).
Figure S16. $^{13}$C NMR of H$_6$1a (CDCl$_3$, 151 MHz).
Figure S17. $^1$H–$^1$H COSY spectrum of H$_6$1a (CDCl$_3$, 600 MHz).

Figure S18. $^1$H–$^1$H ROESY spectrum of H$_6$1a (CDCl$_3$, 600 MHz).
Figure S19. $^1$H–$^{13}$C HSQC spectrum of H$_6$1a (CDCl$_3$, 600 MHz).

Figure S20. $^1$H–$^{13}$C HMBC spectrum of H$_6$1a (CDCl$_3$, 600 MHz).
**Figure S21.** IR spectrum of H$_6$1a (KBr)

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Figure S22. $^1$H NMR spectrum of 1aZn(OAc)$_6$ (CDCl$_3$, 600 MHz).
Figure S23. $^{13}$C NMR spectrum of 1aZn$_6$(OAc)$_6$ (CDCl$_3$, 151 MHz).
Figure S24. ESI TOF mass spectrum of 1aZn₆(OAc)₆ (positive, CH₃OH/H₂O = 10/1)
Figure S25. A titration experiment of Zn(OAc)$_2$ with H$_6$1a ($^1$H NMR, 400 MHz). A CD$_3$OD solution of Zn(OAc)$_2$ (400 mM) was titrated against a CDCl$_3$ solution of H$_6$1a (2.0 mM). See Figures S15 and S22 for the assignment of $^1$H NMR signals. (a) H$_6$1a. (b–e) H$_6$1a + Zn(OAc)$_2$. (b) Zn(OAc)$_2$ 1.0 eq. (c) 2.0 eq. (d) 3.0 eq. (e) 6.0 eq.
Figure S26. $^1$H NMR spectrum of 1bZn$_6$(OAc)$_6$ (CDCl$_3$, 400 MHz)
A single crystal of [1bZn₆(H₂O)₆(OAc)₄]-2(C₄H₈O)-1.5(C₄H₁₀O) suitable for an X-ray diffraction analysis was obtained by the slow diffusion of Et₂O vapor into a THF solution of 1bZn₆(H₂O)₁₁(OAc)₆. Some of the acetate ligands, THF and Et₂O solvent molecules were solved with DFIX and RIGU restraints. Solvent accessible voids of 1634 cubic angstroms (10.0% of the unit cell, probe radius 1.2 angstrom) were found, where acetate anions and solvent molecules (tetrahydrofuran and diethyl ether) were heavily disordered. Residual electron densities due to the disordered molecules were not fully determined.

Crystal data for [1bZn₆(H₂O)₆(OAc)₄]-2(C₄H₈O)-1.5(C₄H₁₀O): C₁₃₀H₁₄₅N₁₂O₂₃.5Zn₆, \( F_w = 2643.79 \), purple plate, 0.63 × 0.35 × 0.04 mm³, monoclinic, space group \( P 2_1/n \) (No. 14), \( a = 17.605(8) \) Å, \( b = 37.882(17) \) Å, \( c = 24.680(11) \) Å, \( \beta = 97.040(5)^\circ \), \( V = 16335(13) \) Å³, \( Z = 4 \), \( R_1 = 0.1672 \), \( wR_2 = 0.4345 \), GOF = 2.328. CCDC 1884373.

Figure S27. The molecular structure of [1bZn₆(H₂O)₆(OAc)₄]-2(C₄H₈O)-1.5(C₄H₁₀O) determined by X-ray diffraction analysis. An ellipsoidal model (50% probability). Hydrogen atoms were omitted for clarity. C, light green; N, blue; O, red; Zn, yellow.
Figure S28. $^1$H NMR spectrum of 1aZn$_6$(OTf)$_6$ (CDCl$_3$, 600 MHz)
Figure S29. $^{13}$C NMR spectrum of 1aZn$_6$(OTf)$_6$ (CDCl$_3$, 151 MHz)
Figure S30. $^1$H–$^1$H COSY spectrum of 1aZn$_6$(OTf)$_6$ (CDCl$_3$, 600 MHz)

Figure S31. $^1$H–$^1$H ROESY spectrum of 1aZn$_6$(OTf)$_6$ (CDCl$_3$, 600 MHz)
Figure S32. $^1$H–$^1$H HSQC spectrum of 1aZn$_6$(OTf)$_6$ (CDCl$_3$, 600 MHz)

Figure S33. $^1$H–$^1$C HMBC spectrum of 1aZn$_6$(OTf)$_6$ (CDCl$_3$, 600 MHz)
Figure S34. ESI TOF mass spectrum of 1aZn₆(OTf)₆ (positive, CH₃OH/H₂O = 10/1)
Figure S35. Effect of counter anions in the synthesis of 1aZn₆(OTf)₆ (¹H NMR, 600 MHz, CDCl₃) See Figures S15 and S28 for the assignment of ¹H NMR signals.  
(a) H₆1a.  
(b) H₆1a + 6.0 equivalents of Zn(OTf)₂, and stirred at r.t. for 1 h.  
(c) H₆1a + 3.0 equivalents of Zn(OAc)₂·2H₂O and 3.0 equivalents of Zn(OTf)₂, and stirred at r.t. for 1 h, and dissolution/evaporation in CHCl₃/CH₃OH process for five times.
Figure S36. $^1$H NMR spectrum of 1aZn$_3$Ag$_3$X$_n$ ($X = \text{H}_2\text{O}, \text{AcO}^-$, and TfO$^-$) (CDCl$_3$, 600 MHz)
Figure S37. ESI TOF mass spectrum of 1aZn₃Ag₃Xₙ (X = H₂O, AcO⁻ and TfO⁻) (positive, CH₃OH)
A single crystal of [1aZn₃Ag₃(H₂O)₇(OAc)₂(OTf)₃] suitable for an X-ray diffraction analysis was obtained by the slow diffusion of i-Pr₂O vapor into a CDCl₃ solution of 1aZn₃Ag₃Xₙ. After successive trials, solvent accessible voids of 4485 Å³ in total (calculated by SQUEEZE) were left unfilled, in which solvents (chloroform and diisopropyl ether), counterions (proton, zinc and silver), and counteranions (trifluoromethanesulfonate and acetate) more than those presented in _atom_site_* were supposed to be heavily disordered. The residual electron density was treated with SQUEEZE. The complex according to _chemical_formula_sum has two negative charges. Due to the heavy disorder of solvents and counter ions, its detailed charge state is elusive. DFIX restraints were applied for the atoms of trifluoromethyl groups and disordered cyclohexane rings. Global RIGU and ISOR restraints were also applied during refinement. The complex was derived from a chiral 1R,2R-cyclohexanediame derivative, but the crystal was solved as P₂₁/n space group. The chiral cyclohexanediame part was solved as a disordered pair with half occupancy for each. For the other parts of the complex, no additional disorder is applied. The trial to solve the structure as the chiral P₂₁ space group was not successful, due to too many parameters for full matrix refinement.

Crystal data for 1aZn₃Ag₃(H₂O)₇(OAc)₂(OTf)₃: C₁₁₅H₁₁₄Ag₁₃F₉N₁₂O₂₆S₃Zn₃, Fw = 2881.19, yellow rhombus, 0.19 × 0.18 × 0.10 mm³, monoclinic, space group P₂₁/n (No. 14), a = 21.452(4) Å, b = 20.711(4) Å, c = 35.533(7) Å, β = 99.370(2)°, V = 15576(5) Å³, Z = 4, R₁ = 0.1455, wR₂ = 0.4197, GOF = 2.899. CCDC 1884374.

Figure S38. The molecular structure of [1aZn₃Ag₃(H₂O)₇(OAc)₂(OTf)₃] determined by X-ray diffraction analysis. An ellipsoidal model (50% probability). Hydrogen atoms were omitted for clarity. C, light green; N, blue; O, red; F, yellow green; S, orange; Zn, yellow; Ag, gray.
Table S1. The examination of systematic weaknesses in the diffractions of the crystal of [1aZn$_3$Ag$_3$(H$_2$O)$_7$(OAc)$_2$(OTf)$_3$] performed by WINGX[56], which suggests $P2_1/n$ space group.

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Formation of a double-decker complex

Scheme S11. Synthesis of a double-decker complex 1a:4Zn12(H2O)n(O Tf)12 (5).

1aZn6(H2O)22(O Tf)6 (4.02 mg, 1.20 µmol) and CDCl3 (500 µL) were added to a NMR tube, which resulted in a clear yellow solution. Next, 1,4-diazabicyclo[2,2,2]octane (3.27 mg, 29.15 µmol) and CDCl3 (250 µL) were added to a microtube. Three portions of the 1,4-diazabicyclo[2,2,2]octane solution (5.5 µL, 0.64 µmol) were added to the NMR tube and the clear yellow mixture was shaken by hand at room temperature for 1 minute. The solvent was evaporated and the yellow residue was dried under vacuum to give 5 (4.2 mg, quantitative).

Yellow solid;
1H NMR (600 MHz, CDCl3): δ 8.04 (s, 6H), 7.93 (s, 6H), 7.10 (s, 6H), 7.08 (s, 6H), 6.98 (s, 6H), 6.96 (s, 6H), 6.94 (s, 12H), 4.01 (br, 6H), 3.26–3.08 (br, 36H), 2.89 (br, 6H), 2.35 (s, 6H), 2.34 (s, 6H), 2.03 (s, 6H), 1.98 (s, 6H), 1.84 (s, 6H), 1.80 (s, 6H), 1.75–1.65 (30H), 1.40 (br, 6H), 1.09 (br, 6H), 0.78 (br, 6H);
19F NMR; (565 MHz, CDCl3): δ -78.6 (br), -79.4 (br).
UV (CDCl3): λmax 413 nm (ε = 2.7 × 105 [M⁻¹·cm⁻¹]); FL (CDCl3) λmax 467, 491 nm (λex = 413 nm);
Emission quantum yield: Φε = 0.30 (λex = 413 nm);
See Figure S47 for the ESI TOF-MS spectrum.
**Figure S39.** $^1$H NMR spectra of 1,4-diazabicyclo[2,2,2]octane titration (DABCO (4), 0 – 3.4 eq) against 1aZn$_6$(OTf)$_6$ (2 mM) (CDCl$_3$, 600 MHz)

1aZn$_6$(H$_2$O)$_{22}$(OTf)$_6$ (3.18 mg, 0.95 µmol) and CDCl$_3$ (500 µL) were added to an NMR tube, which gave a clear yellow solution. Next, 1,4-diazabicyclo[2,2,2]octane (7.31 mg, 65.16 µmol) and CDCl$_3$ (1.00 mL) were added to a microtube. The 1,4-diazabicyclo[2,2,2]octane solution was added to the NMR tube 6 times in 8.25 µL (0.59 µmol) portions. The titration was monitored by $^1$H NMR spectroscopy.
Figure S40. $^1$H NMR spectrum of a double-decker complex 5 (CDCl$_3$, 600 MHz)
Figure S41. $^{19}$F NMR spectrum of a double-decker complex 5 (CDCl$_3$, 565 MHz)

Figure S42. $^1$H–$^1$H COSY spectrum of a double-decker complex 5. (CDCl$_3$, 600 MHz)
Figure S43. $^1$H–$^1$H ROESY spectrum of a double-decker complex 5. (CDCl$_3$, 600 MHz)

Figure S44. $^1$H–$^{13}$C HSQC spectrum of a double-decker complex 5. (CDCl$_3$, 600 MHz)
Figure S45. $^1$H–$^{13}$C HMBC spectrum of a double-decker complex 5. (CDCl$_3$, 600 MHz)

Figure S46. $^1$H DOSY spectrum of a double-decker complex 5. (CDCl$_3$, 600 MHz)
Figure S47. ESI TOF mass spectrum of a double-decker complex $1\text{a}_2\text{Zn}_{12}\text{Zn}_{4}(\text{H}_2\text{O})_{6+}\!(\text{OH})_6\!(\text{H}_2\text{O})_2\text{OTf}_{12}$ (5).
A single crystal of $[1a_24_3\text{Zn}_{12}(\text{H}_2\text{O})_{12}]\text{(OTf)}_{12}$ suitable for an X-ray diffraction analysis was obtained by the slow diffusion of cyclohexane vapor into a AcOMe solution of $[1a_24_3\text{Zn}_{12}X_6]\text{(OTf)}_{12}$. The crystal structure was refined as a 2-component twin related by the matrix (010 100 00-1). After successive trials, solvent accessible voids of 12809 Å$^3$ in total (calculated by SQUEEZE) were left unfilled, in which solvents (cyclohexane, methyl acetate, and water) and counter ions (trifluoromethanesulfonate) more than those presented in _atom_site_* were supposed to be heavily disordered. The residual electron density was treated with SQUEEZE. Due to the heavy disorder of solvents and counter ions, the detailed charge state of the complex is elusive. DFIX restraints and global RIGU and SIMU restraints were applied during refinement. The complex was derived from a chiral 1R,2R-cyclohexanediamine derivative, but the crystal was solved as solved as the P-6 space group. The chiral cyclohexanediamine part was solved as a disordered pair with a half occupancy for each one. DABCO was disordered with a half occupancy in the crystal. Due to the disorder of the bridging DABCO as well as TfO$^-$ anions, the reflections with $l \neq 0$ were weak like a two-dimensional crystal. Considering these features and the fact that the complex is a derivative of the chiral 1R,2R-cyclohexanediamine, the true space group might be P3.

Crystal data: $C_{117.33}H_{126}N_{15}O_{6}Zn_{6}$, $F_w = 2234.54$, orange prism, hexagonal, space group P-6 (No. 174), $a = 44.628(3)$ Å, $c = 17.071(4)$ Å, $V = 29445(4)$ Å$^3$, $Z = 6$, $R_1 = 0.1140$, $wR_2 = 0.3396$, GOF = 1.080. CCDC 1884375.

**Figure S48.** The crystal structure of $[1a_24_3\text{Zn}_{12}(\text{H}_2\text{O})_{12}]$ determined by X-ray diffraction analysis. An ellipsoidal model (30% probability). Hydrogen atoms were omitted for clarity. C, light green; N, blue; O, red; Zn, yellow.
Table S2. The examination of systematic weaknesses in the diffractions of the crystal of [1a2.4Zn12(H2O)12] performed by WINGX[86].

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Absorption, emission, and circular dichroism spectra

It was confirmed by $^1$H NMR measurement that the formation ratio of $\text{1a}_{2}\text{4}_{2}\text{Zn}_{12}(\text{OTf})_{12}$ is above 90% at 55 mM, the concentration used for the measurements in Figures S49–S51.

Figure S49. Absorption spectra of $\text{H}_6\text{1a}$ and its complexes. Conditions: ($\text{H}_6\text{1a}$, $\text{1aZn}_6(\text{OAc})_6$ and $\text{1aZn}_3\text{Ag}_3(\text{OAc})_m(\text{OTf})_n$) CHCl$_3$, 10 μM, $l = 1$ cm; $\text{1aZn}_6(\text{OTf})_6$, CHCl$_3$, 110 μM, $l = 1$ mm; $\text{1a}_{2}\text{4}_{2}\text{Zn}_{12}(\text{OTf})_{12}$, CDCl$_3$, 55 μM, $l = 1$ mm.
**Figure S50.** Normalized emission spectra of H$_6$1a and its complexes. Conditions: H$_6$1a, CHCl$_3$, 10 µM, $\lambda_{ex}$ = 360 nm; 1aZn$_6$(OAc)$_6$, CHCl$_3$, 10 µM, $\lambda_{ex}$ = 420 nm; 1aZn$_3$Ag$_3$(OAc)$_m$(OTf)$_n$, CHCl$_3$, 10 µM, $\lambda_{ex}$ = 411 nm; 1aZn$_6$(OTf)$_6$, CHCl$_3$, 110 µM, $\lambda_{ex}$ = 413 nm; 1a$_2$4$_3$Zn$_{12}$(OTf)$_{12}$, CDCl$_3$, 55 µM, $\lambda_{ex}$ = 413 nm.
Figure S51. Circular dichroism spectra of H$_6$1a and its complexes. Conditions: (H$_6$1a, 1aZn$_6$(OAc)$_6$ and 1aZn$_3$Ag$_3$(OAc)$_m$(OTf)$_n$) CHCl$_3$, 10 µM, $l$ = 1 cm; 1aZn$_6$(OTf)$_6$, CHCl$_3$, 110 µM, $l$ = 1 mm; 1a$_2$4$_3$Zn$_{12}$(OTf)$_{12}$, CDCl$_3$, 55 µM, $l$ = 1 mm.
References for the Supporting Information