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Supporting Information

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Intramolecular [3 + 2] Annulation in 5-Ary-20-ethynyl-substituted [26]Hexaphyrin(1.1.1.1.1.1) Triggered by Molecular Compression via Dynamic Conformational Change

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I. General Information

All reagents and solvents were of the commercial reagent grade and were used without further purification except where noted. ^{1}H NMR spectra were recorded on a JEOL ECA-600 spectrometer, (operating as 600.17 MHz for ^{1}H, 600.17 MHz for ^{13}C, and 564.73 MHz for ^{19}F) using the residual solvent in $CDCl_3$ and CD_2Cl_2 as the internal reference for ^{1}H (d = 7.26 and 5.30 respectively), $CDCl_3$ as the internal reference for ^{13}C (d = 77.0), and hexafluorobenzene as external reference for ^{19}F (d = –162.9 ppm). The spectroscopic grade CH_2Cl_2 was used as solvents for all spectroscopic studies. UV/visible absorption was recorded on a Shimadzu UV-3100 spectrometer. Mass spectra were recorded on a BRUKER microTOF using positive and negative mode ESI-TOF methods of acetonitrile solutions. Preparative separations were performed by silica gel gravity column chromatography (Wako gel C-400). The Solid-state magnetic susceptibility was measured between 2 and 300 K under a magnetic field of 0.5 T with a SQUID magnetometer (Quantum Design MPMS-1).

II. Experimental Section

General procedure of 5-aryl-20-ethynyl hexaphyrin (3a-e)

To a solution of TIPS-propargyl aldehyde **5** (105 mg, 0.50 mmol), benzaldehyde (0.50 mmol) and 5,10-bis(pentafluorophenyl) tripyrrane **4** (558 mg, 1.0 mmol) in CH_2Cl_2 (44 ml) was added methanesulfonic acid (2.5 M diluted with CH_2Cl_2, 25 μL) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred for 2 h and then DDQ (1.0 g) was added. After further stirring for 1 h at room temperature, the resulting solution was passed through a short basic-alumina column with MeOH/CH_2Cl_2 (1:9) and the solvent was removed by a rotary evaporator. The residual mixture was purified by silica gel column chromatography with CH_2Cl_2/hexane (in an appropriate ratio) as an eluent. 5-aryl-20-ethynyl hexaphyrin **3** was eluted just after 5,20-bisethynyl hexaphyrin **1** as deep blue fraction. After removal of solvent, the resulting solids were recrystalized from a mixture of CH_2Cl_2/MeOH, giving 5-aryl-20-ethynyl-hexaphyrin **3** as gold solids.

General procedure of spiro-indenylene macrocycle (6a-c)

A solution of 5-aryl-20-ethynyl hexaphyrin **3** in toluene was refluxed for 12 h. Spiro-indenylene macrocycle **6** was quantitatively obtained as purple solids after removal of solvent.

General procedure of spiro-indenylene macrocycle (6d-j)

To a solution of propalgyl aldehyde (0.50 mmol), aryl aldehyde (0.50 mmol) and 5,10-bis(pentafluorophenyl) tripyrrane **4** (558 mg, 1.0 mmol) in CH_2Cl_2 (44 ml) was added methanesulfonic acid (2.5 M diluted with CH_2Cl_2, 25 μL) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred for 2 h and then DDQ (1.0 g) was added. After further stirring for 1 h at room temperature, the resulting solution was passed through a short basic-alumina column with MeOH/CH_2Cl_2 (1:9) and the solvent was removed by a rotary evaporator. The residual mixture was purified by silica gel column chromatography with CH_2Cl_2/hexane (3:7) as an eluent. Spiro-indenylene macrocycle **6** was eluted as red fraction. Spiroindeno-macrocycle **6** was obtained as purple solids after removal of solvent.

5-pheny-10,15,25,30-tetrakis(pentafluorophenyl)-20-(2-triisopropylsilylethynyl) [26]hexaphyrin(1.1.1.1.1.1) (3a): 32 mg, Yield 4.9%. ^{1}H-NMR ($CDCl_3$): *d* = -2.22 (d, *J* = 4.1 Hz, 2H, inner *b*-H), -2.19 (d, *J* = 4.6 Hz, 2H, outer *b*-H), -1.96 (br, 1H, NH), -1.43 (br, 1H, NH), 1.50 (d,

J = 6.9 Hz, 18H, TIPS-primary), 1.57 (m, 3H, TIPS-tertiary), 7.92 (m, 3H, phenyl-*meta, para*), 8.36 (d, *J* = 7.8 Hz, 1H, phenyl-*ortho*), 9.11 (d, *J* = 4.6 Hz, 2H, outer *b*-H), 9.24 (d, *J* = 4.6 Hz, 2H, outer *b*-H), 9.38 (d, *J* = 4.6 Hz, 2H, outer *b*-H), and 9.89 (d, *J* = 4.6 Hz, 2H, outer *b*-H) ppm; ^{19}F-NMR ($CDCl_3$): *d* = -163.24 (t, *J* = 17.5 Hz, 4F, *meta*-F), -163.11 (t, *J* = 17.5 Hz, 4F, *meta*-F), -153.35 (t, *J* = 26.3 Hz, 2F, *para*-F), -153.08 (t, *J* = 26.3 Hz, 2F, *para*-F), -136.98 (d, *J* = 26.3 Hz, 4F, *ortho*-F), and -136.90 (d, *J* = 17.6 Hz, 4F, *ortho*-F) ppm; UV/vis (CH_2Cl_2): l_{max} (*e* [$M^{-1}cm^{-1}$]): 1040 (13000), 909 (5700), 797 (17000), 734 (23000), and 577 (260000) nm; ESI-TOF-Mass (positive-mode) (%intensity): $C_{71}H_{41}F_{20}N_6Si$ ([*M*+H]$^+$), calcd: 1285.2837, found: 1385.2839 (100%).

5-(4-methoxyphenyl)-10,15,25,30-tetrakis(pentafluorophenyl)-20-(2-triisopropylsilylethynyl) [26]hexaphyrin(1.1.1.1.1.1) (3b): 72 mg, Yield 10%. ^{1}H-NMR ($CDCl_3$): *d* = -2.11 (d, *J* = 4.1 Hz, 2H, inner *b*-H), -2.09 (d, *J* = 4.6 Hz, 2H, outer *b*-H), -1.84 (br, 1H, NH), -1.26 (br, 1H, NH), 1.49-1.60 (21H, TIPS), 4.16 (s, 3H, methoxy), 7.44 (d, *J* = 8.3 Hz, 2H, phenyl-*meta*), 8.28 (d, *J* = 8.7 Hz, 2H, phenyl-*ortho*), 9.12 (d, *J* = 4.6 Hz, 2H, outer *b*-H), 9.22 (d, *J* = 4.6 Hz, 2H, outer *b*-H), 36 (d, *J* = 4.6 Hz, 2H, outer *b*-H), and 9.86 (d, *J* = 4.6 Hz, 2H, outer *b*-H) ppm; ^{19}F-NMR ($CDCl_3$): *d* = -163.27 (br, 4F, *meta*-F), -163.13 (br, 4F, *meta*-F), -153.42 (t, *J* = 17.6 Hz, 2F, *para*-F), -153.16 (t, *J* = 17.6 Hz, 2F, *para*-F), -137.01 (d, *J* = 26.3 Hz, 4F, *ortho*-F), and -136.92 (d, *J* = 17.6 Hz, 4F, *ortho*-F) ppm; UV/vis (CH_2Cl_2): l_{max} (*e* [$M^{-1}cm^{-1}$]): 1039 (14000), 904 (6900), 802 (21000), 737 (25000), and 578 (310000) nm; ESI-TOF-Mass (positive-mode) (%intensity): $C_{72}H_{43}F_{20}N_6SiO$ ([*M*+H]$^+$), calcd: 1415.2943, found: 1415.2944 (100%).

5-(2,4-dimethoxyphenyl)-10,15,25,30-tetrakis(pentafluorophenyl)-20- (2-triisopropylsilylethynyl) [26]hexaphyrin(1.1.1.1.1.1) (3c): 57 mg, Yield 7.9%. ^{1}H-NMR ($CDCl_3$): *d* = -2.39 (d, *J* = 4.1 Hz, 2H, inner *b*-H), -2.35 (d, *J* = 4.1 Hz, 2H, outer *b*-H), -2.13 (br, 1H, NH), -1.73 (br, 1H, NH), 1.50-1.62 (21H, TIPS), 3.75 (s, 3H, methoxy), 4.16 (s, 3H, methoxy), 7.00 (d, *J* = 2.3 Hz, 1H, phenyl-*meta*), 7.04 (dd, *J* = 2.3, 2.8 Hz, 1H, phenyl-*meta*), 8.06 (d, *J* = 8.3 Hz, 1H, phenyl-*ortho*), 9.12 (d, *J* = 4.6 Hz, 2H, outer *b*-H), 9.24 (d, *J* = 4.6 Hz, 2H, outer *b*-H), 9.41 (d, *J* = 5.0 Hz, 2H, outer *b*-H), and 9.92 (d, *J* = 4.6 Hz, 2H, outer *b*-H) ppm; ^{19}F-NMR ($CDCl_3$): *d* = -163.28 (m, 8F, *meta*-F), -153.45 (m, 4F, *para*-F), -137.18 (br, 4F, *ortho*-F), -136.71 (d, *J* = 26.3 Hz, 4F, *ortho*-F), and -136.57 (d, *J* = 26.3 Hz, 4F, *ortho*-F) ppm; UV/vis (CH_2Cl_2): l_{max} (*e* [$M^{-1}cm^{-1}$]): 1043 (16000), 800 (18000), 739 (24000), and 579 (290000) nm; ESI-TOF-Mass (positive-mode) (%intensity): $C_{73}H_{45}F_{20}N_6SiO_2$ ([*M*+H]$^+$), calcd: 1445.3048, found: 1445.3044 (100%).

5-(2,4,6-trimethoxyphenyl)-10,15,25,30-tetrakis(pentafluorophenyl)-20- (2-triisopropylsilylethynyl) [26]hexaphyrin(1.1.1.1.1.1) (3d): 53 mg, Yield 7.2%. ^{1}H-NMR ($CDCl_3$): *d* = -2.56 (d, *J* = 4.1 Hz, 2H, inner *b*-H), -2.51 (d, *J* = 4.1 Hz, 2H, outer *b*-H), -2.293 (br, 1H, NH), -1.99 (br, 1H, NH), 1.53 (d, *J* = 6.8 Hz, 18H, TIPS-primary), 1.60 (m, 3H, TIPS-tertiary), 3.68 (s, 6H, *o*-methoxy), 4.17 (s, 3H, *p*-methoxy), 6.69 (s, 2H, phenyl-*meta*), 9.15 (d, *J* = 4.6 Hz, 2H, outer *b*-H), 9.27 (d, *J* = 4.6 Hz, 2H, outer *b*-H), 9.45 (d, *J* = 4.6 Hz, 2H, outer *b*-H), and 9.97 (d, *J* = 4.6 Hz, 2H, outer *b*-H) ppm; ^{19}F-NMR ($CDCl_3$): *d* = -163.47 (t, *J* = 26.3 Hz, 2F, *meta*-F), -163.35 (t, *J* = 17.5 Hz, 2F, *meta*-F), -153.70 (m, 4F, *para*-F), -136.91 (d, *J* = 26.3 Hz, 4F, *ortho*-F), and -136.82 (d, *J* = 17.5 Hz, 4F, *ortho*-F) ppm; UV/vis (CH_2Cl_2): l_{max} (*e* [$M^{-1}cm^{-1}$]): 1041 (13000), 800 (15000), 7359 (21000), and 579 (240000) nm; ESI-TOF-Mass (positive-mode) (%intensity): $C_{74}H_{47}F_{20}N_6SiO_3$ ([*M*+H]$^+$), calcd: 1475.3154, found: 1445.3159 (100%).

5-(2,6-dichlorophenyl)-10,15,25,30-tetrakis(pentafluorophenyl)-20-(2-triisopropylsilylethynyl) [26]hexaphyrin(1.1.1.1.1.1) (3e): 25 mg, Yield 3.4%. ^{1}H-NMR ($CDCl_3$): *d* = -2.49 (d, *J* = 4.6 Hz, 2H, inner *b*-H), -2.41 (d, *J* = 4.6 Hz, 2H, outer *b*-H), -2.17 (br, 1H, NH), -2.04 (br, 1H, NH), 1.50-1.62 (21H, TIPS), 7.85 (t, *J* = 8.8 Hz, 1H, phenyl-*para*), 7.93 (d, *J* = 8.7 Hz, 2H, phenyl-*meta*), 8.97 (d, *J* = 4.6 Hz, 2H, outer *b*-H), 9.22 (d, *J* = 5,0 Hz, 2H, outer *b*-H), 9.43 (d, *J* = 4.6 Hz, 2H, outer *b*-H), and 9.96 (d, *J* = 4.6 Hz, 2H, outer *b*-H) ppm; ^{19}F-NMR ($CDCl_3$): *d* = -163.16 (br, 8F, *meta*-F), -153.19 (m, 4F, *para*-F), -136.97 (d, *J* = 26.3 Hz, 4F, *ortho*-F), and -136.71 (d, *J* = 26.3 Hz, 4F, *ortho*-F) ppm; UV/vis (CH_2Cl_2): l_{max} (*e* [$M^{-1}cm^{-1}$]): 1043 (15000), 794 (15000), 730 (23000), and 574 (240000) nm; ESI-TOF-Mass (positive-mode) (%intensity): $C_{71}H_{39}F_{20}N_6SiCl_2$ ([*M*+H]$^+$), calcd: 1455.2059, found: 1455.2054 (100%).

Spiro-indenylene macrocycle 6a : ^{1}H-NMR ($CDCl_3$): *d* = 0.57 (d, *J* = 7.2 Hz, 9H, TIPS-primary), 0.60 (d, *J* = 7.2 Hz, 9H, TIPS-primary), 0.83 (m, 3H, TIPS-tertiary), 6.16 (m, 1H, *b*-H), 6.21 (m, 1H, *b*-H), 6.36 (d, *J* = 4.8 Hz, 1H, *b*-H), 6.50 (m, 1H, *b*-H), 6.52 (d, *J* = 7.8 Hz, 1H, benzene-ring), 6.74 (d, *J* = 4.8 Hz, 1H, *b*-H), 6.81 (m, 1H, *b*-H), 6.82 (d, *J* = 7.2 Hz, 1H, benzene-ring), 6.91 (m, 1H, *b*-H), 6.92 (t, *J* = 6.6 Hz, 1H, benzene-ring), 6.97 (d, *J* = 4.2 Hz, 1H, *b*-H), 7.06 (t, *J* = 7.2 Hz, 1H, benzene-ring), 7.38 (dd, *J* = 3.0 Hz 4.2 Hz, 1H, *b*-H), 7.50 (d, *J* = 5.4 Hz, 1H, *b*-H), 7.80 (dd, *J* = 1.8 Hz 6.0 Hz, 1H, *b*-H), 7.86 (d, *J* = 5.4 Hz, 1H, *b*-H), 9.39 (s, 1H, NH), 9.66 (s, 1H, NH), and 13.02 (s, 1H, NH) ppm; ^{19}F-NMR ($CDCl_3$): *d* = -160.80 (m, 8F, *meta*-F), -152.73 (t, *J* = 17.6 Hz, 1F, *para*-F), -152.23 (t, *J* = 26.3 Hz, 1F, *para*-F), -152.10 (t, *J* = 17.5 Hz, 1F, *para*-F), -151.71 (t, *J* = 26.3 Hz, 1F, *para*-F), -138.35 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -138.10 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -

137.82 (m, 2F, *ortho*-F), -137.52 (m, 2F, *ortho*-F), -137.30 (d, *J* = 26.3 Hz, 1F, *ortho*-F), and -137.13 (d, *J* = 26.3 Hz, 1F, *ortho*-F) ppm; ^{13}C-NMR ($CDCl_3$): 13.15, 18.89, 18.96, 67.02, 96.80, 111.27, 115.71, 117.38, 117.89, 118.60, 119.99, 120.52, 120.87, 121.04, 121.49, 125.33, 127.22, 127.57, 128.20, 128.51, 130.13, 131.83, 133.89, 134.11, 135.50, 136.51, 137.91, 139.42, 143.68, 145.41, 146.22, 151.98, 152.52, 152.63, 154.01, 154.84, 155.41, 165.14, 167.08, and 172.10 ppm; l_{max} (e [$M^{-1}cm^{-1}$]) : 932 (16000), 844 (14000), 561 (46000), and 420 (58000) nm; ESI-TOF-Mass (positive-mode) (%intensity): $C_{71}H_{41}F_{20}N_6Si$ ([*M*+H]$^+$), calcd: 1385.2837, found: 1385.2832 (100%).

Spiro-indenylene macrocycle 6b : ^{1}H-NMR ($CDCl_3$): *d* = 0.55 (d, *J* = 7.3 Hz, 9H, TIPS-primary), 0.58 (d, *J* = 7.3 Hz, 9H, TIPS-primary), 0.81 (m, 3H, TIPS-tertiary), 6.17 (m, 1H, *b*-H), 6.21 (m, 1H, *b*-H), 6.31 (d, *J* = 2.0 Hz, 1H, benzene-ring), 6.37 (d, *J* = 4.5 Hz, 1H, *b*-H), 6.43 (m, 2H, benzene-ring), 6.49 (m, 1H, *b*-H), 6.75 (d, *J* = 4.8 Hz, 1H, *b*-H), 6.81 (d, *J* = 5.5 Hz, 1H, *b*-H), 6.92 (d, *J* = 4.8 Hz, 1H, *b*-H), 6.96 (d, *J* = 4.5 Hz, 1H, *b*-H), 7.36 (dd, *J* = 2.9 Hz 3.8 Hz, 1H, *b*-H), 7.49 (d, *J* = 5.1 Hz, 1H, *b*-H), 7.80 (dd, *J* = 1.9 Hz 5.5 Hz, 1H, *b*-H), 7.84 (d, *J* = 4.5 Hz, 1H, *b*-H), 9.33 (s, 1H, NH), 9.58 (s, 1H, NH), and 13.00 (s, 1H, NH) ppm; ^{19}F-NMR ($CDCl_3$): *d* = -160.81 (m, 8F, *meta*-F), -152.76 (t, *J* = 17.6 Hz, 1F, *para*-F), -152.26 (t, *J* = 17.6 Hz, 1F, *para*-F), -152.13 (t, *J* = 17.6 Hz, 1F, *para*-F), -151.76 (t, *J* = 17.6 Hz, 1F, *para*-F), -138.37 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -138.11 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -137.83 (m, 2F, *ortho*-F), -137.62 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -137.53 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -137.26 (d, *J* = 17.6 Hz, 1F, *ortho*-F), and -137.16 (d, *J* = 17.6 Hz, 1F, *ortho*-F) ppm; UV/vis (CH_2Cl_2): l_{max} (e [$M^{-1}cm^{-1}$]): 935 (17000), 833 (16000), 558 (47000), and 422 (65000) nm; ESI-TOF-Mass (positive-mode) (%intensity): $C_{72}H_{43}F_{20}N_6SiO$ ([*M*+H]$^+$), calcd: 1415.2943, found: 1415.2945 (100%).

Spiro-indenylene macrocycle 6c : ^{1}H-NMR ($CDCl_3$): *d* = 0.63 (d, *J* = 7.7 Hz, 9H, TIPS-primary), 0.65 (d, *J* = 7.4 Hz, 9H, TIPS-primary), 0.92 (m, 3H, TIPS-tertiary), 3.41 (s, 3H, methoxy), 3.61 (s, 3H, methoxy), 6.00 (d, *J* = 1.6 Hz, 1H, benzene-ring), 6.08 (m, 1H, *b*-H), 6.12 (m, 1H, *b*-H), 6.13 (d, *J* = 1.9 Hz, 1H, benzene-ring), 6.31 (d, *J* = 4.4 Hz, 1H, *b*-H), 6.41 (m, 1H, *b*-H), 6.69 (d, *J* = 4.5 Hz, 1H, *b*-H), 6.72 (d, *J* = 5.1 Hz, 1H, *b*-H), 6.78 (d, *J* = 4.5 Hz, 1H, *b*-H), 6.84 (d, *J* = 4.8 Hz, 1H, *b*-H), 7.30 (m, 1H, *b*-H), 7.39 (d, *J* = 4.8 Hz, 1H, *b*-H), 7.69 (dd, *J* = 1.6 Hz 5.4 Hz, 1H, *b*-H), 7.75 (d, *J* = 4.8 Hz, 1H, *b*-H), 9.69 (s, 1H, NH), 9.85 (s, 1H, NH), and 13.39 (s, 1H, NH) ppm; ^{19}F-NMR ($CDCl_3$): *d* = -160.92 (m, 8F, *meta*-F), -152.97 (t, *J* = 17.5 Hz, 1F, *para*-F), -152.49 (t, *J* = 17.6 Hz, 1F, *para*-F), -152.34 (t, *J* = 17.6 Hz, 1F, *para*-F), -152.12 (t, *J* = 17.5 Hz, 1F, *para*-F), -138.42 (d, *J*

= 17.6 Hz, 1F, *ortho*-F), -138.09 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -137.97 (m, 2F, *ortho*-F), -137.72 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -137.53 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -137.43 (d, *J* = 17.5 Hz, 1F, *ortho*-F), and -137.24 (d, *J* = 26.3 Hz, 1F, *ortho*-F) ppm; UV/vis (CH_2Cl_2): l_{max} (*e* [$M^{-1}cm^{-1}$]): 930 (15000), 848 (14000), 559 (41000), and 427 (60000) nm; ESI-TOF-Mass (positive-mode) (%intensity): $C_{73}H_{45}F_{20}N_6SiO_2$ ([*M*+H]$^+$), calcd: 1445.3048, found: 1445.3050 (100%).

Spiro-indenylene macrocycle 6f : 27 mg, Yield 3.8%. ^{1}H-NMR ($CDCl_3$): *d* = 0.51 (d, *J* = 7.3 Hz, 9H, TIPS-primary), 0.53 (d, *J* = 7.4 Hz, 9H, TIPS-primary), 0.74 (m, 3H, TIPS-tertiary), 3.36 (s, 3H, methoxy), 3.52 (s, 3H, methoxy), 5.70 (d, *J* = 1.9 Hz, 1H, benzene-ring), 6.01 (d, *J* = 1.9 Hz, 1H, benzene-ring), 6.17 (m, 1H, *b*-H), 6.24 (m, 1H, *b*-H), 6.43 (d, *J* = 4.8 Hz, 1H, *b*-H), 6.54 (m, 1H, *b*-H), 6.80 (d, *J* = 4.5 Hz, 1H, *b*-H), 6.82 (d, *J* = 5.4 Hz, 1H, *b*-H), 6.90 (d, *J* = 4.5 Hz, 1H, *b*-H), 6.97 (d, *J* = 4.4 Hz, 1H, *b*-H), 7.38 (m, 1H, *b*-H), 7.50 (d, *J* = 4.8 Hz, 1H, *b*-H), 7.79 (dd, *J* = 1.6 Hz 5.4 Hz, 1H, *b*-H), 7.84 (d, *J* = 4.8 Hz, 1H, *b*-H), 9.16 (s, 1H, NH), 9.46 (s, 1H, NH), and 13.09 (s, 1H, NH) ppm; ^{19}F-NMR ($CDCl_3$): *d* = -161.13 (br, 4F, *meta*-F), -160.86 (m, 4F, *meta*-F), -153.08 (t, *J* = 17.5 Hz, 1F, *para*-F), -152.51 (t, *J* = 17.6 Hz, 1F, *para*-F), -152.35 (t, *J* = 26.3 Hz, 1F, *para*-F), -151.93 (t, *J* = 26.3 Hz, 1F, *para*-F), -138.17 (d, *J* = 17.5 Hz, 1F, *ortho*-F), -137.93 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -137.69 (m, 4F, *ortho*-F), and -137.35 (m, 2F, *ortho*-F) ppm; UV/vis (CH_2Cl_2): l_{max} (*e* [$M^{-1}cm^{-1}$]): 938 (14000), 842 (13000), 557 (44000), and 427 (55000) nm; ESI-TOF-Mass (positive-mode) (%intensity): $C_{73}H_{45}F_{20}N_6SiO_2$ ([*M*+H]$^+$), calcd: 1445.3048, found: 1445.3049 (100%).

Spiro-indenylene macrocycle 6g : 55 mg, Yield 7.5%. ^{1}H-NMR ($CDCl_3$): *d* = 0.53 (d, *J* = 7.4 Hz, 9H, TIPS-primary), 0.55 (d, *J* = 7.7 Hz, 9H, TIPS-primary), 0.88 (m, 3H, TIPS-tertiary), 6.12 (m, 1H, *b*-H), 6.17 (m, 1H, *b*-H), 6.38 (d, *J* = 4.5 Hz, 1H, *b*-H), 6.59 (d, *J* = 8.3 Hz, 1H, naphthalene-ring), 6.60 (m, 1H, *b*-H), 6.76 (d, *J* = 4.8 Hz, 1H, *b*-H), 6.91 (d, *J* = 5.7 Hz, 1H, *b*-H), 6.98 (d, *J* = 4.5 Hz, 2H, *b*-H), 7.13 (dd, *J* = 7.2 Hz 5.6 Hz, 1H, naphthalene-ring), 7.24 (t, *J* = 8.0 Hz, 1H, naphthalene-ring), 7.35 (d, *J* = 8.3 Hz, 1H, naphthalene-ring), 7.51 (dd, *J* = 2.5 Hz 4.2 Hz, 1H, *b*-H), 7.60 (d, *J* = 8.0 Hz, 1H, naphthalene-ring), 7.65 (d, *J* = 4.8 Hz, 1H, *b*-H), 7.91 (d, *J* = 8.6 Hz, 1H, naphthalene-ring), 7.95 (m, 1H, *b*-H), 9.03 (s, 1H, NH), 9.33 (s, 1H, NH), and 13.09 (s, 1H, NH) ppm; ^{19}F-NMR ($CDCl_3$): *d* = -160.99 (m, 4F, *meta*-F), -160.72 (m, 4F, *meta*-F), -152.77 (t, *J* = 17.6 Hz, 1F, *para*-F), -152.27 (t, *J* = 17.5 Hz, 1F, *para*-F), -152.10 (t, *J* = 17.5 Hz, 1F, *para*-F), -151.76 (t, *J* = 17.6 Hz, 1F, *para*-F), -138.33 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -138.10 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -137.84 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -137.83 (br, 3F, *ortho*-F), and -137.16 (br, 2F, *ortho*-F) ppm; UV/vis (CH_2Cl_2): l_{max} (*e* [$M^{-1}cm^{-1}$]): 937 (17000), 847 (16000), 554 (46000), and 424

(65000) nm; ESI-TOF-Mass (positive-mode) (%intensity): $C_{75}H_{43}F_{20}N_6Si$ ([*M*+H]$^+$), calcd: 1435.2994, found: 1435.2997 (100%).

Spiro-indenylene macrocycle 6h : 46 mg, Yield 6.5%. ^{1}H-NMR ($CDCl_3$): *d* = 0.61 (d, *J* = 7.4 Hz, 9H, TIPS-primary), 0.64 (d, *J* = 7.7 Hz, 9H, TIPS-primary), 0.85 (m, 3H, TIPS-tertiary), 6.15 (m, 1H, *b*-H), 6.17 (d, *J* = 5.2 Hz, 1H, thiophene-ring), 6.22 (m, 1H, *b*-H), 6.34 (d, *J* = 4.8 Hz, 1H, *b*-H), 6.43 (m, 1H, *b*-H), 6.72 (d, *J* = 4.5 Hz, 1H, *b*-H), 6.76 (d, *J* = 5.4 Hz, 1H, *b*-H), 6.89 (d, *J* = 4.8 Hz, 1H, *b*-H), 6.92 (d, *J* = 4.5 Hz, 1H, *b*-H), 7.02 (d, *J* = 4.8 Hz, 1H, thiophene-ring), 7.23 (dd, *J* = 2.5 Hz 3.5 Hz, 1H, *b*-H), 7.37 (d, *J* = 4.8 Hz, 1H, *b*-H), 7.65 (dd, *J* = 1.6 Hz 5.46 Hz, 1H, *b*-H), 7.72 (d, *J* = 4.6 Hz, 1H, *b*-H), 9.82 (s, 1H, NH), 10.06 (s, 1H, NH), and 13.15 (s, 1H, NH) ppm; ^{19}F-NMR ($CDCl_3$): *d* = -160.91 (m, 5F, *meta*-F), -160.64 (m, 3F, *meta*-F), -152.74 (t, *J* = 26.3 Hz, 1F, *para*-F), -152.22 (t, *J* = 17.5 Hz, 1F, *para*-F), -152.10 (t, *J* = 26.3 Hz, 1F, *para*-F), -151.74 (t, *J* = 26.3 Hz, 1F, *para*-F), -138.40 (d, *J* = 17.5 Hz, 1F, *ortho*-F), -138.06 (d, *J* = 17.5 Hz, 1F, *ortho*-F), -137.86 (d, *J* = 17.6 Hz, 1F, *ortho*-F), -137.80 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -137.63 (m, 2F, *ortho*-F), and -137.22 (m, 2F, *ortho*-F) ppm; UV/vis (CH_2Cl_2): l_{max} (*e* [$M^{-1}cm^{-1}$]): 934 (16000), 848 (15000), 556 (43000), and 419 (68000) nm; ESI-TOF-Mass (positive-mode) (%intensity): $C_{69}H_{39}F_{20}N_6SiS$ ([*M*+H]$^+$), calcd: 1391.2401, found: 1391.2394 (100%).

Spiro-indenylene macrocycle 6i : 10 mg, Yield 1.6%. ^{1}H-NMR ($CDCl_3$): *d* = 6.15 (m, 1H, *b*-H), 6.19 (m, 1H, *b*-H), 6.39 (d, *J* = 4.6 Hz, 1H, *b*-H), 6.53 (m, 1H, *b*-H), 6.76 (d, *J* = 4.6 Hz, 1H, *b*-H), 6.83-7.15 (9H, phenyl, benzene-ring, *b*-H), 7.49 (m, 1H, *b*-H), 7.54 (m, 2H, benzene-ring, *b*-H), 7.80 (m, 2H, benzene-ring, *b*-H), 7.82 (dd, *J* = 1.8 Hz 5.7 Hz, 1H, *b*-H), 7.84 (d, *J* = 4.6 Hz, 1H, *b*-H), 9.27 (s, 1H, NH), 9.88 (s, 1H, NH), and 13.04 (s, 1H, NH) ppm; ^{19}F-NMR ($CDCl_3$): *d* = -160.81 (br, 4F, *meta*-F), -160.60 (br, 4F, *meta*-F), -152.66 (t, *J* = 17.5 Hz, 1F, *para*-F), -152.03 (t, *J* = 26.3 Hz, 1F, *para*-F), -151.93 (m, 2F, *para*-F), -151.62 (t, *J* = 26.3 Hz, 1F, *para*-F), -137.53 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -137.40 (m, 3F, *ortho*-F), -137.23 (m, 3F, *ortho*-F), and -136.90 (d, *J* = 17.6 Hz, 1F, *ortho*-F) ppm; UV/vis (CH_2Cl_2): l_{max} (*e* [$M^{-1}cm^{-1}$]): 925 (18000), 843 (18000), 558 (56000), and 420 (71000) nm; ESI-TOF-Mass (positive-mode) (%intensity): $C_{68}H_{24}F_{20}N_6Na$ ([*M*+Na]$^+$), calcd: 1327.1635, found: 1327.1633 (100%).

Spiro-indenylene macrocycle 6j : 39 mg, Yield 5.7%. ^{1}H-NMR ($CDCl_3$): *d* = 6.15 (m, 1H, *b*-H), 6.17 (m, 1H, *b*-H), 6.42 (d, *J* = 4.6 Hz, 1H, *b*-H), 6.60 (m, 1H, *b*-H), 6.80 (d, *J* = 4.6 Hz, 1H, *b*-H), 6.82-6.98 (9H, phenyl, naphthalene-ring, *b*-H), 7.19 (t, *J* = 8.2 Hz, 1H, naphthalene-ring), 7.30 (t, *J*

= 8.2 Hz, 1H, naphthalene-ring), 7.45 (d, *J* = 8.2 Hz, 1H, naphthalene-ring), 7.56 (dd, *J* = 2.8 Hz 4.1 Hz, 1H, *b*-H), 7.64 (d, *J* = 4.6 Hz, 1H, *b*-H), 7.66 (d, *J* = 8.6 Hz, 1H, naphthalene-ring), 7.88 (d, *J* = 5.0 Hz, 1H, *b*-H), 7.91 (dd, *J* = 1.8 Hz 5.7 Hz, 1H, *b*-H), 8.10 (d, *J* = 8.7 Hz, 1H, naphthalene-ring), 9.06 (s, 1H, NH), 9.66 (s, 1H, NH), and 13.20 (s, 1H, NH) ppm; ^{19}F-NMR ($CDCl_3$): *d* = -160.88 (br, 4F, *meta*-F), -160.60 (br, 4F, *meta*-F), -152.69 (t, *J* = 26.3 Hz, 1F, *para*-F), -152.03 (t, *J* = 26.3 Hz, 1F, *para*-F), -151.89 (t, *J* = 17.5 Hz, 1F, *para*-F), -151.60 (t, *J* = 17.6 Hz, 1F, *para*-F), -137.67 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -137.47 (d, *J* = 17.6 Hz, 1F, *ortho*-F), -137.27 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -137.16 (br, 3F, *ortho*-F), and -137.84 (m, 2F, *ortho*-F) ppm; UV/vis (CH_2Cl_2): λ_{max} (*e* [$M^{-1}cm^{-1}$]): 922 (17000), 850 (18000), 555 (54000), 423 (70000), and 323 (41000) nm; ESI-TOF-Mass (positive-mode) (%intensity): $C_{72}H_{27}F_{20}N_6$ ([*M*+H]$^+$), calcd: 1355.1972, found: 1355.1975 (100%).

Spiro-indenylene macrocycle bis-zinc complex 7a : A solution of **6a** (13.5 mg, 0.00975 mmol) and $ZnCl_2$ (400 mg) in MeOH and the resulting solution was heated at reflux. After 5 h, the reaction mixture was diluted with CH_2Cl_2 and passed through silica gel column with MeOH in CH_2Cl_2 (5%) as an eluent. After removal of solvent, **7a** was obtained as purple solids. (15 mg, 0.0097 mmol, quant.). ^{1}H-NMR (CD_2Cl_2): *d* = 0.09 (d, *J* = 6.8 Hz, 9H, TIPS-primary), 0.15 (d, *J* = 6.1 Hz, 9H, TIPS-primary), 0.68 (m, 3H, TIPS-tertiary), 6.33 (d, *J* = 7.4 Hz, 1H, benzene-ring), 6.55 (m, 2H, *b*-H), 6.78 (d, *J* = 4.2 Hz 1H, *b*-H), 6.89 (d, *J* = 4.1 Hz, 1H, *b*-H), 6.98 (t, *J* = 6.4 Hz, 1H, benzene-ring), 7.07 (d, *J* = 7.7 Hz, 1H, benzene-ring), 7.12 (t, *J* = 7.4 Hz, 1H, benzene-ring), 7.22 (d, *J* = 4.8 Hz, 1H, *b*-H), 7.26 (s, *2*H, *b*-H), 7.42 (d, *J* = 3.8 Hz, 1H, *b*-H), 7.97 (d, *J* = 4.1 Hz, 1H, *b*-H), 8.11 (d, *J* = 4.8 Hz, 1H, *b*-H), 8.13 (d, *J* = 3.8 Hz, 1H, *b*-H), and 8.23 (d, *J* = 4.1 Hz, 1H, *b*-H) ppm; ^{19}F-NMR ($CDCl_3$): *d* = -161.33 (br, 2F, *meta*-F), 160.64 (br, 2F, *meta*-F), -160.47 (br, 2F, *meta*-F), 160.30 (br, 2F, *meta*-F), -152.07 (br, 3F, *para*-F), -151.61 (br, 1F, *para*-F), -138.62 (br, 2F, *ortho*-F), -138.17 (br, 1F, *ortho*-F), -138.03 (br, 1F, *ortho*-F), -137.89 (br, 1F, *ortho*-F), and -135.69 (m, 2F, *ortho*-F) ppm; UV/vis (CH_2Cl_2): l_{max} (*e* [$M^{-1}cm^{-1}$]): 1156 (33000), 1005 (15000), 631 (47000), 478 (87000), and 324 (20000) nm; ESI-TOF-Mass (positive-mode) (%intensity): $C_{71}H_{37}F_{20}N_6SiZn_2$ ([*M*-Cl]$^+$), calcd: 1513.1083, found: 1513.1084 (100%).

Spiroindeno-macrocycle bis-zinc complex 7g : A solution of **6e** (20 mg, 0.014 mmol) and $ZnCl_2$ (200 mg) in MeOH and the resulting solution was heated at reflux. After 5 h, the reaction mixture was diluted with CH_2Cl_2 and passed through silica gel column with MeOH in CH_2Cl_2 (5%) as an eluent. After removal of solvent, the residual mixture was separated by silica gel column

chromatography with MeOH/CH_2Cl_2 (3:97 v/v) as an eluent to afford **7g** (21 mg, 0.013 mmol, 94%). ^{1}H-NMR (CD_2Cl_2): *d* = 0.10 (br, 18H, TIPS-primary), 0.24 (m, 3H, TIPS-tertiary), 6.33~8.29 (*b*-H and naphthalene-ring) ppm; ^{19}F-NMR ($CDCl_3$): *d* = -161.36 (br, 2F, *meta*-F), -160.78 (br, 2F, *meta*-F), -160.57 (br, 2F, *meta*-F), -152.10 (br, 3F, *para*-F), -151.68 (br, 1F, *para*-F), -138.62 (br, 2F, *ortho*-F), -138.24 (d, *J* = 26.3 Hz, 1F, *ortho*-F), -138.00 (br, 2F, *ortho*-F), -137.69 (d, *J* = 17.5 Hz, 1F, *ortho*-F), -135.48 (d, *J* = 26.3 Hz, 1F, *ortho*-F), and -135.09 (d, *J* = 26.3 Hz, 1F, *ortho*-F) ppm; UV/vis (CH_2Cl_2): l_{max} (*e* [$M^{-1}cm^{-1}$]): 1157 (35000), 1009 (10000), 624 (40000), 478 (85000), and 330 (27000) nm; ESI-TOF-Mass (positive-mode) (%intensity): $C_{75}H_{39}F_{20}N_6SiZn_2$ ([*M*-Cl]$^+$), calcd: 1563.1241, found: 1563.1242 (100%).

Spiroindeno-macrocycle bis-copper complex 8a : 6a (40 mg, 0.029 mmol) was reacted with CuCl (400 mg) in a mixed solvent of MeOH/CH_2Cl_2 (5ml/15ml) for 1 h. The reaction was terminated by passing through short alumina column with CH_2Cl_2 as an eluent. After removal of solvent, recrystalization from a mixture of MeOH/CH_2Cl_2 gave **8a** as purple solids (37 mg, 0.024 mmol, Yield 84%). UV/vis (CH_2Cl_2): l_{max} (*e* [$M^{-1}cm^{-1}$]): 1243 (12000), 664 (29000), 619 (30000), and 448 (84000) nm; ESI-TOF-Mass (positive-mode) (%intensity): $C_{71}H_{37}F_{20}N_6SiCu_2$ ([*M*]$^+$), calcd: 1509.1119, found: 1509.1120 (100%).

III. Figures and Schemes

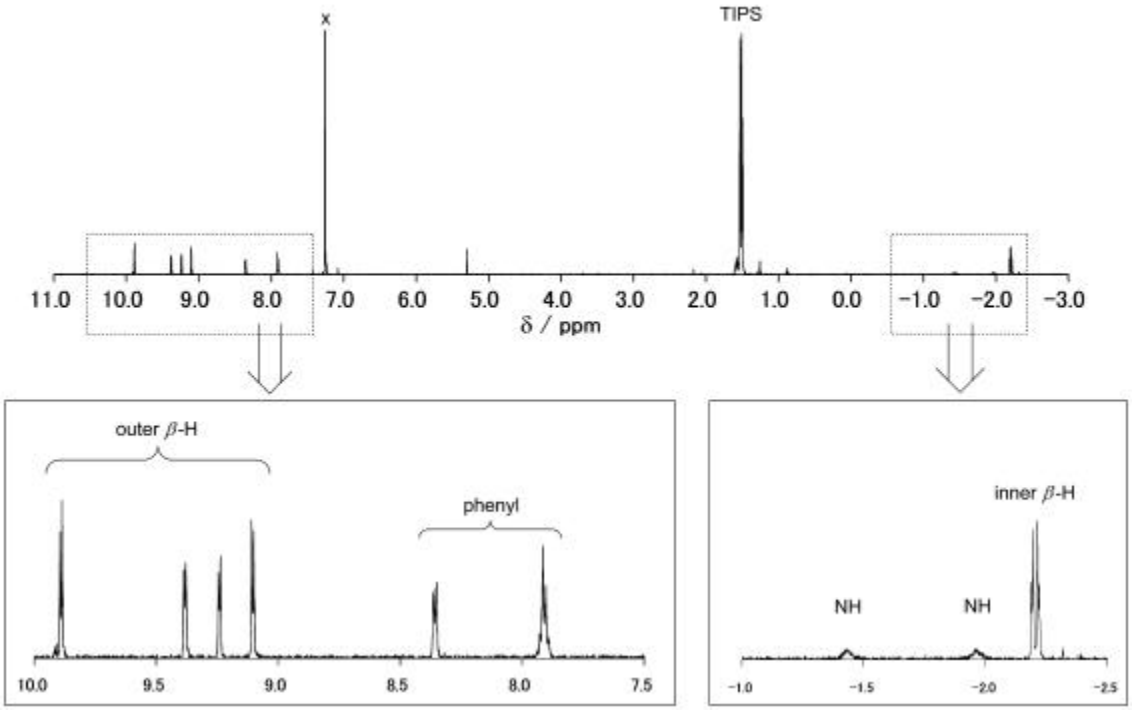


Figure S1. ^{1}H NMR spectrum of **3a** in $CDCl_3$.

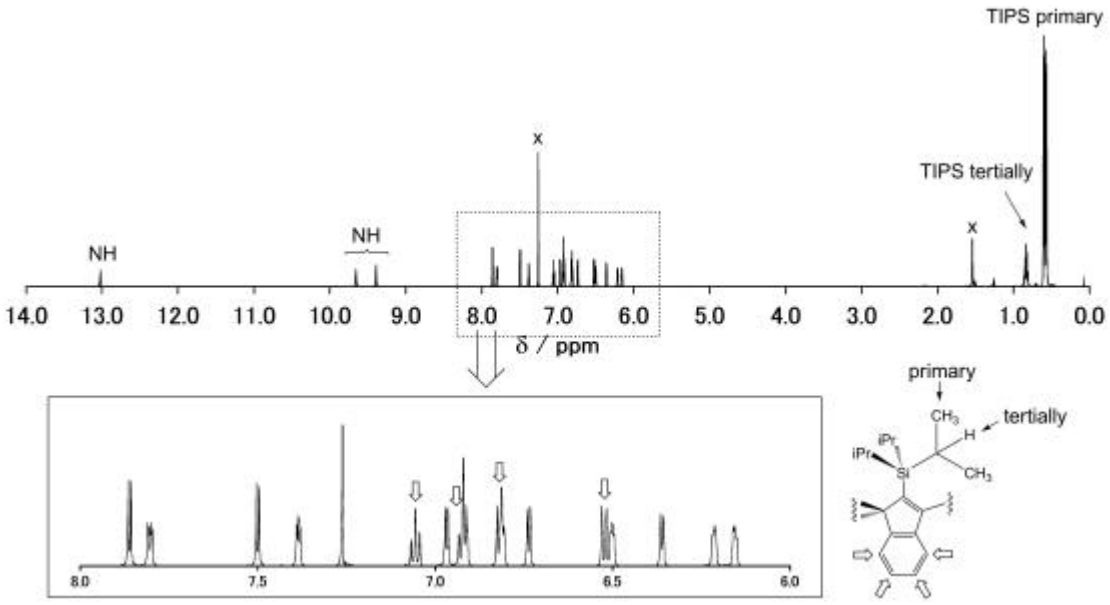


Figure S2. ^{1}H NMR spectrum of **6a** in $CDCl_3$.

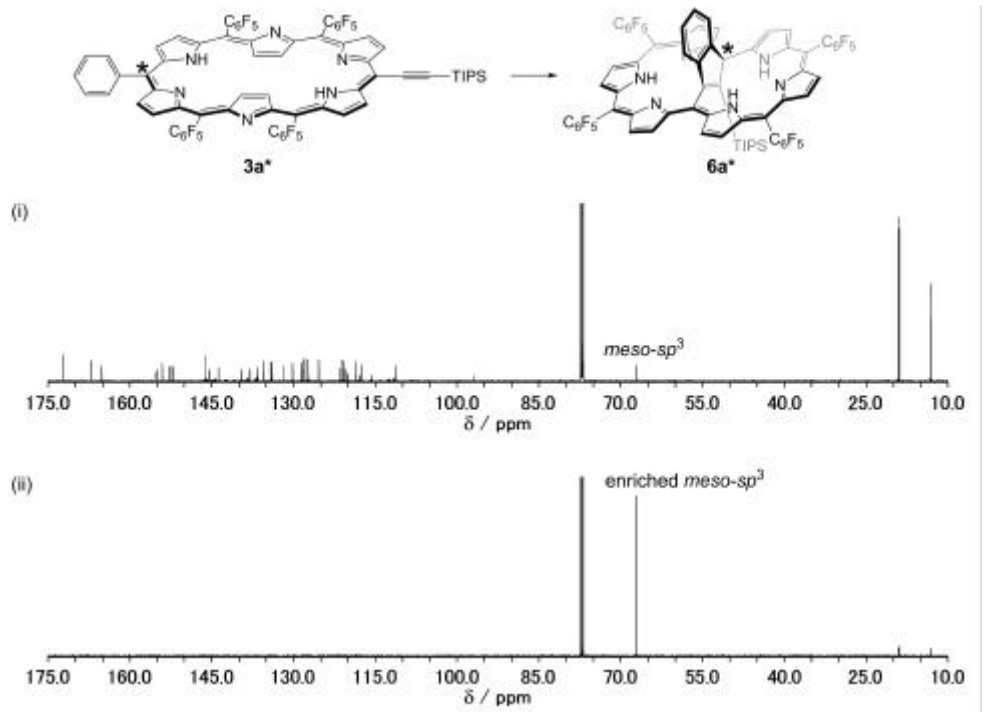


Figure S3. ^{13}C NMR spectrum of i) **6a** and ii) **6a*** in $CDCl_3$. **3a*** was prepared with benzaldehyde-*carbonyl*-^{13}C.

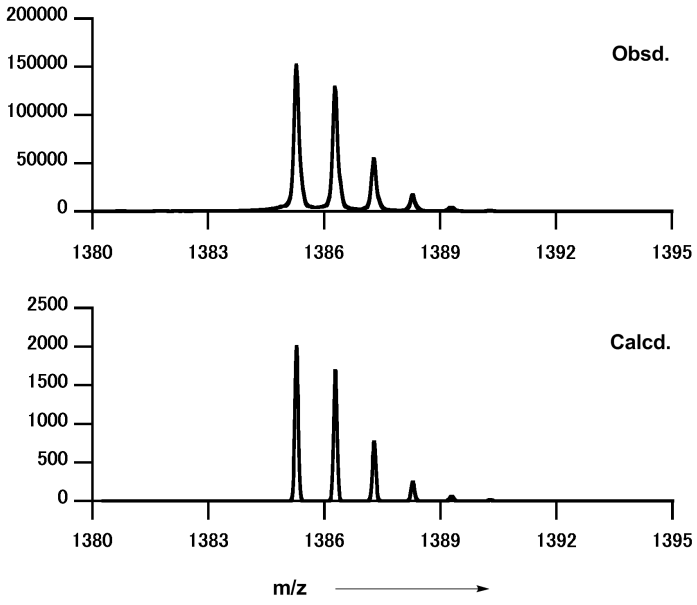


Figure S4. HR-ESI-TOF mass spectrum of **3a**. Upper: obsd; lower: calcd.

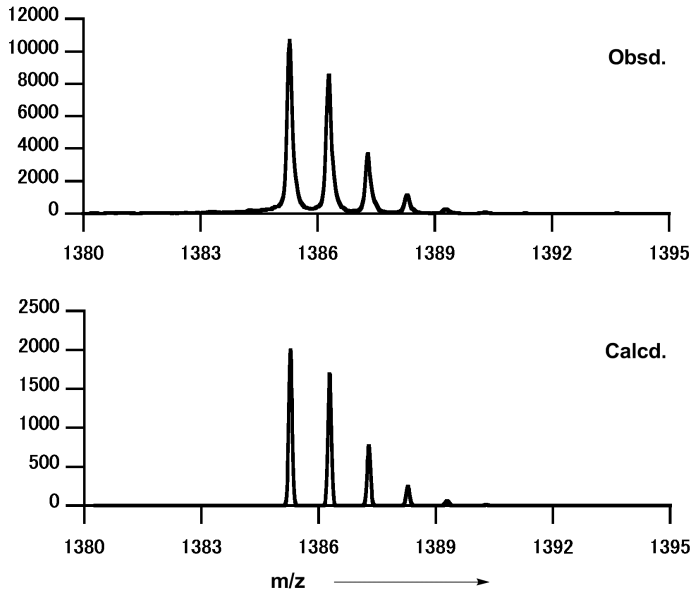


Figure S5. HR-ESI-TOF mass spectrum of **6a**. Upper: obsd; lower: calcd.

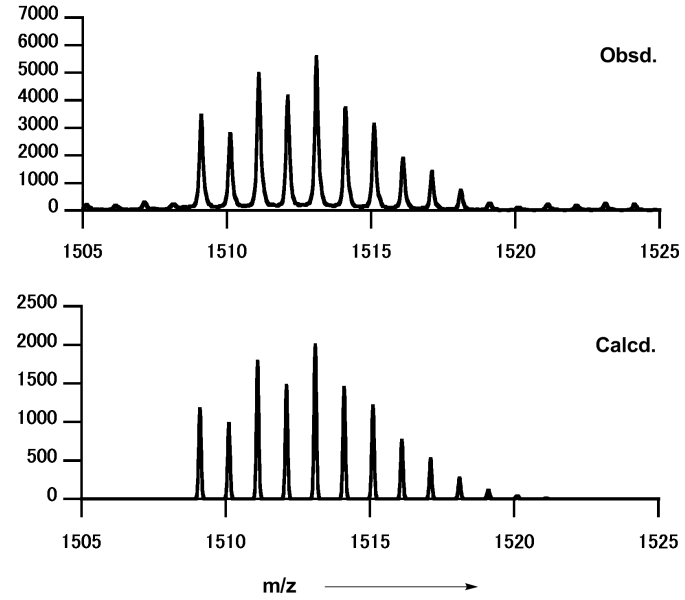


Figure S6. HR-ESI-TOF mass spectrum of **7a**. Upper: obsd; lower: calcd.

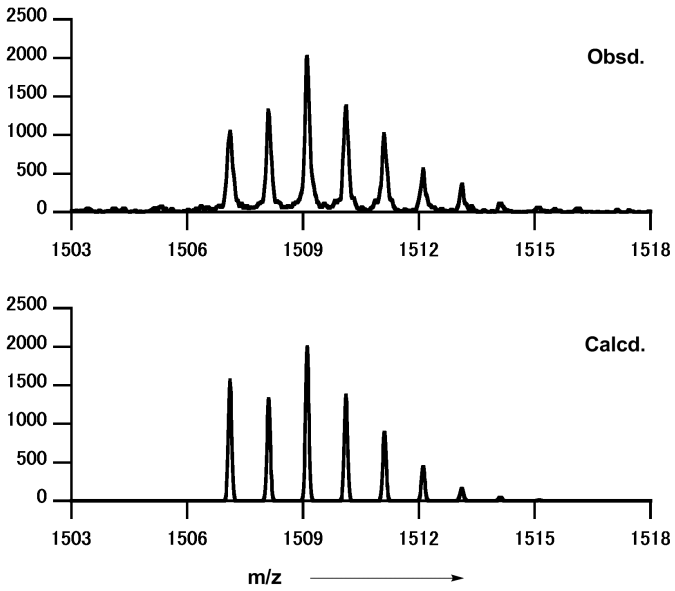


Figure S7. HR-ESI-TOF mass spectrum of **8a**. Upper: obsd; lower: calcd.

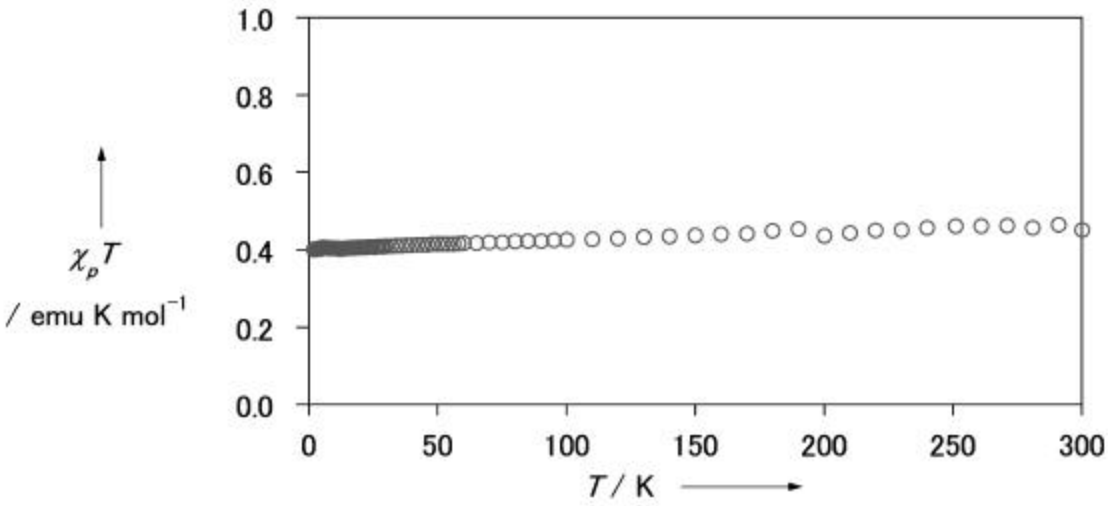


Figure S8. Temperature dependent magnetic susceptibility of **8a**.

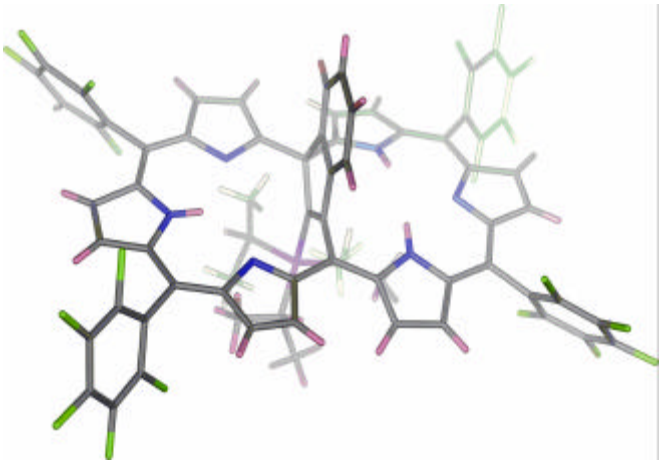


Figure S9. Full representative oblique view of **6a**.

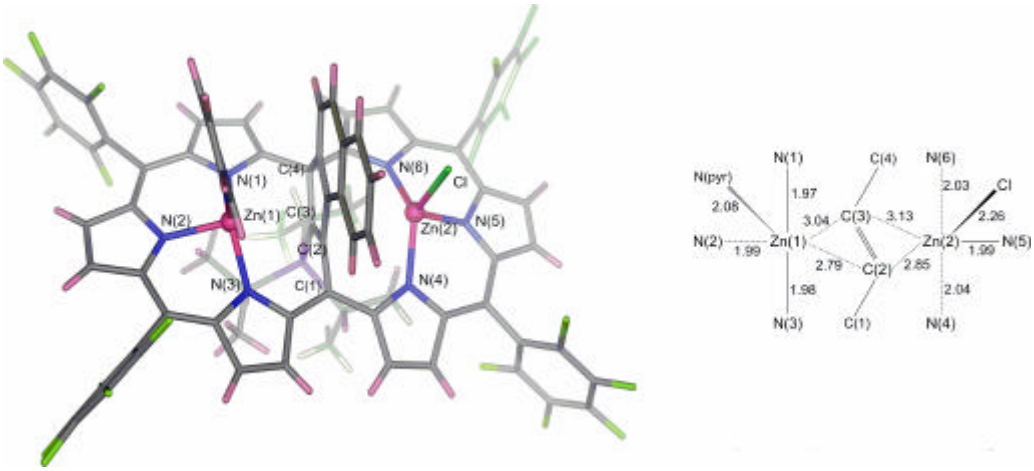


Figure S10. Full representative oblique view and bond distances around zinc ions of **7g**.

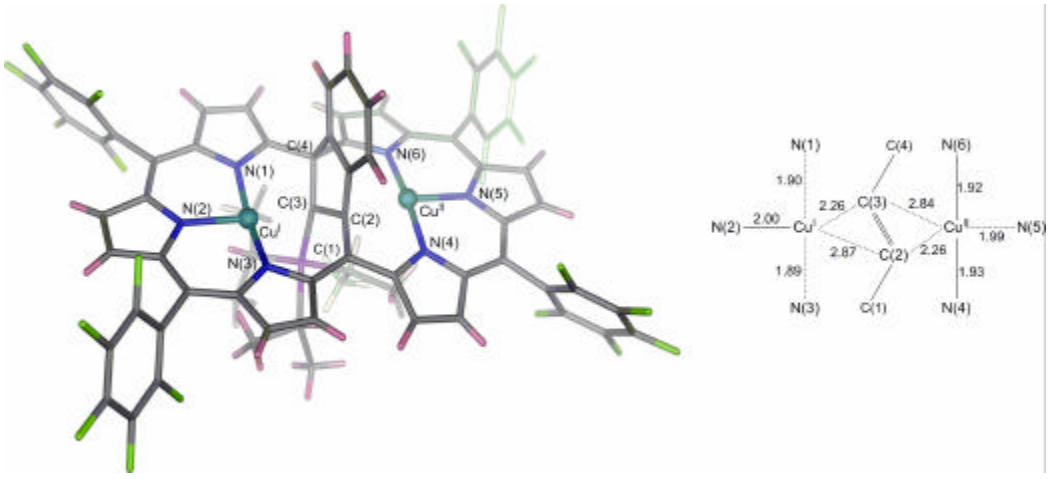


Figure S11. Full representative oblique view and bond distances around copper ions of **8a**.

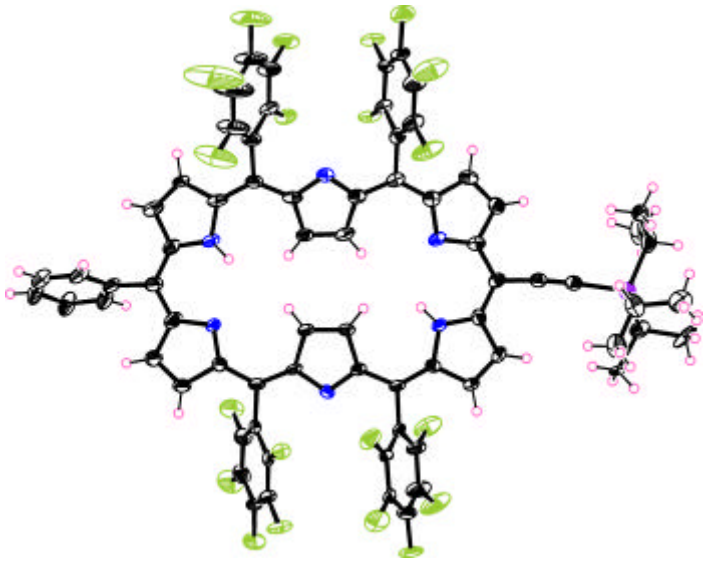
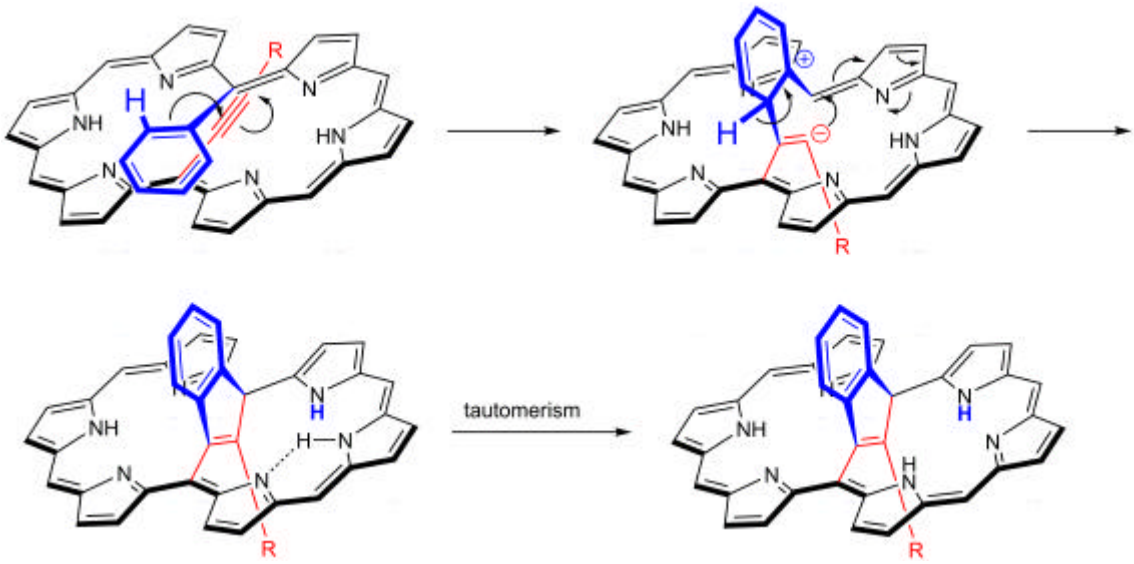


Figure S12. Preliminary crystal structure of **3a**. Crystal data: orthorhombic, space group *Pbca* (No. 61), a = 35.153, b = 24.678, c = 14.537 Å, Z = 8, R_1 = 0.149 ($I > 2s(I)$), R_W = 0.345 (all data).



Scheme S1. A possible mechanism of conversion of **3** into **6**.