Supporting Information

for

Remote control of the reversible assembly/disassembly of supramolecular aggregates

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Abbreviations:
DCM : dichloromethane
1 Synthesis

General Information

All commercial reagents (compound 7, from Alfa Aesar) were used without further purification. Solvents were dried using the appropriate desiccants and distilled prior to use. $^1$H NMR and $^{13}$C NMR were recorded on a Bruker Avance 400 MHz using the deuterated solvent as the lock and residual protiated solvent as the internal reference (CD$_2$Cl$_2$: $\delta_H = 5.32$ ppm and $\delta_C = 53.8$ ppm). The following abbreviations were utilized to describe peak patterns: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, br = broad, bs = broad singlet, bd = broad doublet and m = multiplet. The numbering of the carbon atoms in the molecular formulae (vide infra) is used only for the assignments of the NMR signals and thus is not necessarily in accordance with IUPAC nomenclature. Electrospray ionization mass spectra (ESI-MS) were recorded on a Thermo-Quest LCQ Deca. UV-vis spectra were recorded on a Cary Win 50 (298 K) spectrometer. Melting points were measured on a Büchi SMP-20 instrument. Infrared spectra were recorded using a Varian 1000 FT-IR instrument. Elemental analysis was done on the EA 3000 CHNS. Ligands 1, 3, 4, 5, 6, 8, 9 were synthesized according to known procedures.

Chart 1: Chemical structures of compounds 1-9.
Synthetic Procedures

Synthesis of ligand 2

3-Ethynyl-2,9-dimesityl-1,10-phenanthroline (8, 50.0 mg, 113 µmol) and 1,4-bis(decyloxy)-2,5-diiodobenzene (13, 36.4 mg, 56.7 µmol) were dissolved in a mixture of dry DMF (10 mL) and dry Et3N (10 mL). The solution was trice subjected to freeze-pump-thaw cycles for removing atmospheric oxygen. Then, Pd(PPh3)4 (6.55 mg, 5.67 µmol) was added into the mixture under N2 atmosphere and subjected to heating at 80 °C for overnight. The reaction mixture was then cooled and solvents were evaporated under reduced pressure. The crude mixture was purified by column chromatography eluting with 5% ethyl acetate in n-hexane on silica gel (Rf = 0.37, 5% ethyl acetate in n-hexane) to furnish a yellow solid in 60% yield. Mp >250 °C. 1H NMR (400 MHz, CD2Cl2) δ 8.47 (s, 2H, 4′-H), 8.32 (d, 3J = 8.0 Hz, 2H, 7′-H), 7.91 (d, 3J = 8.8 Hz, 2H, [5′/6′]-H), 7.86 (d, 3J = 8.8 Hz, 2H, [6′/5′]-H), 7.56 (d, 3J = 8.0 Hz, 2H, 8′-H), 6.98 (s, 4H, [9′/10′]-H), 6.95 (s, 4H, [10′/9′]-H), 6.37 (s, 2H, p-H), 3.85 (t, 3J = 6.4 Hz, 4H, q-H), 2.35 (s, 6H, [12′/14′]-H), 2.33 (s, 6H, [14′/12′]-H), 2.05 (s, 12H, [11′/13′]-H), 2.04 (s, 12H, [13′/11′]-H), 1.84-1.77 (m, 4H, r-H), 1.59-1.22 (m, 28H, -(CH2)7-H), 0.82 (t, 3J = 7.2 Hz, 6H, s-H); 13C NMR (100 MHz, CD2Cl2) δ 161.9, 160.9, 153.4, 146.4, 145.4, 138.8, 138.4, 137.8, 137.6, 137.6, 136.4, 146.1, 128.6, 128.2, 127.9, 127.3, 127.3, 126.0, 125.1, 120.2, 117.5, 114.1, 92.5, 91.9, 69.8, 32.3, 30.2, 30.0, 29.9, 29.8, 29.6, 26.5, 23.0, 21.4, 21.2, 20.4, 20.1, 14.2; ESI-MS: m/z (%) 1267.8 (100) [M+H]+; Anal. Calcd. for C90H80N4O2: C, 85.27; H, 7.79; N, 4.42; found: C, 84.91; H, 7.75; N, 4.31.
Synthesis of complex $[\text{Cu(1)}]^+$

$[\text{Cu(CH}_3\text{CN)}_4]\text{PF}_6$ (123 µg, 0.329 µmol) and molecular switch 1 (360 µg, 0.329 µmol) were taken in a NMR tube directly and dissolved in 500 µL of CD$_2$Cl$_2$. The resultant mixture was subjected to analytical characterization without any purification. Yield: Quantitative; $^1$H NMR (400 MHz, 298 K, CD$_2$Cl$_2$): $\delta = 8.65$ (d, $^3J = 8.0$ Hz, 1 H, 7/4-H), 8.63 (d, $^3J = 8.0$ Hz, 1 H, 4/7-H), 8.19 (s, 2 H, 5-, 6-H), 8.03 (dd, $^3J = 4.6$ Hz, $^4J = 1.2$ Hz, 1 H, a-H), 7.80 (td, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, 1 H, c-H), 7.77 (d, $^3J = 8.4$ Hz, 2 H, 3-, 8-H), 7.66-7.72 (m, 3 H, d-, m-, p-H), 7.60-7.64 (m, 3 H, g-, j-, f-H), 7.51 (s, 4 H, k-, l-H), 7.46-7.48 (m, 2 H, n-, o-H), 7.40-7.42 (m, 2 H, h-, i-H), 7.31 (ddd, $^3J = 8.0$ Hz, $^3J = 4.8$ Hz, $^4J = 1.2$ Hz, 1 H, e-H), 7.29 (d, $^3J = 8.4$ Hz, 1 H, b-H), 7.29 (d, $^3J = 8.4$ Hz, 1 H, c-H), 6.43 (s, 1 H, 10/9-H), 6.35 (s, 1 H, 9/10-H), 4.92 (bs, 1 H, Fc-H), 4.54 (bs, 1 H, Fc-H), 3.89 (bs, 5 H, Fc-H), 3.67 (bs, 1 H, Fc-H), 3.32 (bs, 1 H, Fc-H), 2.17 (s, 3 H, duMe-H), 1.97 (s, 3 H, mesMe-H), 1.78 (s, 3 H, mesMe-H), 1.73 (s, 3 H, duMe-H), 1.68 (s, 3 H, duMe-H), 1.65 (s, 3 H, mesMe-H), 1.53 (s, 3 H, duMe-H) ppm.
**Synthesis**\(^7\) of complex \([\text{Zn}(1)_2]^{2+}\)

\[ \text{Zn(OTf)}_2 \text{ (271 \text{ \textmu g, 0.746 \textmu mol}) and molecular switch 1 (816 \text{ \textmu g, 0.746 \textmu mol}) were placed in a 25 mL flask and refluxed in 15 mL of CH}_2\text{Cl}_2/\text{CH}_3\text{CN = 3:1 for 30 min. After removal of the solvent under reduced pressure the resultant mixture was subjected to analytical characterization without any purification. Yield: Quantitative; } \]  \text{1H NMR (400 MHz, 298 K, CD}_2\text{Cl}_2: \text{CD}_3\text{CN (3:1))}: \delta = 9.12 (d, \textsuperscript{3}J = 8.4 \text{ Hz, 1 H, 7/4-H}), 8.92 (d, \textsuperscript{3}J = 8.4 \text{ Hz, 1 H, 4/7-H}), 8.71 (d, \textsuperscript{3}J = 5.2 \text{ Hz, 1 H, a-H}), 8.45 (d, \textsuperscript{3}J = 8.8 \text{ Hz, 1 H, [5/6]-H}), 8.39 (d, \textsuperscript{3}J = 8.8 \text{ Hz, 1 H, [6/5]-H}), 8.20 (td, \textsuperscript{3}J = 8.0 \text{ Hz, } \textsuperscript{4}J = 1.2 \text{ Hz, 1 H, c-H}), 8.17 (d, \textsuperscript{3}J = 8.4 \text{ Hz, 1 H, [3/8]-H}), 8.02 (d, \textsuperscript{3}J = 8.0 \text{ Hz, 1 H, d-H}), 7.93 (d, \textsuperscript{3}J = 8.4 \text{ Hz, 1 H, [8/3]-H}), 7.89 (d, \textsuperscript{3}J = 8.4 \text{ Hz, 1 H, f-H}), 7.81-7.83 (m, 1 H, p-H), 7.74 (ddd, \textsuperscript{3}J = 7.6 \text{ Hz, } \textsuperscript{2}J = 5.2 \text{ Hz, } \textsuperscript{4}J = 1.2 \text{ Hz, 1 H, b-H}), 7.67-7.63 (m, 3 H, g-, j-, m-H), 7.62 (s, 4 H, k-, l-H), 7.58 (d, \textsuperscript{3}J = 8.4 \text{ Hz, 1 H, e-H}), 7.56-7.54 (m, 2 H, h-, i-H), 7.46-7.44 (m, 2 H, n-, o-H), 6.43 (s, 1 H, [10/9]-H), 6.03 (s, 1 H, [9/10]-H), 5.48 (bs, 1 H, Fc-H), 4.37 (bs, 1 H, Fc-H), 3.98 (bs, 5 H, Fc-H), 3.84 (bs, 1 H, Fc-H), 3.35 (bs, 1 H, Fc-H), 2.22 (s, 3 H, mesMe-H), 1.89 (s, 3 H, duMe-H), 1.86 (s, 6 H, duMe-H), 1.83 (s, 3 H, mesMe-H), 1.71 (s, 3 H, duMe-H), 1.53 (s, 3 H, mesMe-H) ppm.
Synthesis of rectangle R $[\text{Cu}_4(2)_2(4)_2]^{2+}$

Ligand 2 (667 µg, 0.526 µmol), ligand 4 (341 µg, 0.526 µmol) and $[\text{Cu(CH}_3\text{CN})_4]\text{PF}_6$ (392 µg, 1.05 µmol) were placed in a 25 mL flask and refluxed in 10 mL of CH$_2$Cl$_2$ for 10 min. After removal of the solvent under reduced pressure the resultant mixture was subjected to analytical characterization without any purification. Yield: Quantitative; $^1\text{H}$ NMR (400 MHz, 298 K, CD$_2$Cl$_2$): $\delta=9.52$ (s, 4 H, d'-H), 8.75 (s, 4 H, 4'-H), 8.68 (d, $^3J=8.0$ Hz, 4 H, 7'-H), 8.20-8.11 (m, 16 H, a', b', 5' & 6']-H), 7.90 (d, $^3J=8.0$ Hz, 4 H, 8'-H), 7.75 (d, $^3J=8.0$ Hz, 4 H, c'-H), 7.14 (s, 4 H, e'-H), 6.62 (s, 8 H, [9'/10']-H), 6.59 (s, 8 H, [10'/9']-H), 6.35 (s, 4 H, p-H), 4.06 (t, $^3J=6.4$ Hz, 8 H, f'-H), 3.71 (t, $^3J=6.4$ Hz, 8 H, q-H), 2.07 (s, 12 H, [12'/14']-H), 2.05 (s, 12 H, [14'/12']-H), 1.93 (s, 24 H, [11'/13']-H), 1.92 (s, 24 H, [13'/11']-H), 1.85-1.78 (m, 8 H, r-H), 1.67-1.61 (m, 8 H, g'-H), 1.54-1.17 (m, 112 H, -(CH$_2$)$_7$ &-(CH$_2$)$_7$-H), 0.84-0.80 (m, 24 H, s & h'-H). ESI-MS: $m/z$ (%) = 1022.1 (100) $[\text{Cu}_4(2)_2(4)_2]^{4+}$, 1411.2 (40) $[\text{Cu}_4(2)_2(4)_2]^{3+}\text{PF}_6$. 
Synthesis of prism P [Cu₆(3)₂(4)₃]⁶⁺

Ligand 3 (667 µg, 0.526 µmol), ligand 4 (341 µg, 0.526 µmol) and [Cu(CH₃CN)₄]PF₆ (392 µg, 1.05 µmol) were placed in a 25 mL flask and refluxed in 10 mL of CH₂Cl₂ for 10 min. After removal of the solvent under reduced pressure the resultant mixture was subjected to analytical characterization without any purification. Yield: Quantitative; ¹H NMR (400 MHz, 298 K, CD₂Cl₂): δ = 9.57 (brs, 6 H, d'-H), 8.77 (s, 6 H, 4''-H), 8.70 (d, 3 J = 8.4 Hz, 6 H, 7''-H), 8.22 (brs, 18 H, a', 5'' & 6''-H), 8.13 (brd, 3 J = 8.0 Hz, 6 H, b'-H), 7.91 (d, 3 J = 8.4 Hz, 6 H, 8''-H), 7.81 (d, 3 J = 8.0 Hz, 6 H, c'-H), 7.11 (s, 6 H, e'-H), 6.63 (brs, 30 H, p'', 9''- & 10''-H), 4.03 (t, 3 J = 6.4 Hz, 12 H, f'-H), 2.14 (s, 18 H, [12'/14']-H), 2.07 (s, 18 H, [14'/12']-H), 1.94 (s, 36 H, [11'/13']-H), 1.88 (s, 36 H, [13'/11']-H), 1.81-1.75 (m, 12 H, g'-H), 1.53-1.40 (m, 12 H, 3×CH₂-H), 1.27-1.12 (m, 72 H, -(CH₂)₆-H), 0.78 (t, 3 J = 7.2 Hz, 18 H, h'-H). ESI-MS: m/z (%) = 1350.9 (100) [Cu₆(3)₂(4)₃](PF₆)₂⁴⁺, 1850.3 (30) [Cu₆(3)₂(4)₂](PF₆)₃³⁺.
2 Regulation of Supramolecular Assemblies by Signaling

Assembly and disassembly of rectangle R by nanoswitch 1

Preparation of state I:

\[ \text{[Cu(CH}_3\text{CN)}_4]\text{PF}_6 \text{ (271 } \mu\text{g, 0.727 } \mu\text{mol) was added to the solution of nanoswitch 1 (795 } \mu\text{g, 0.727 } \mu\text{mol), ligand 2 (461 } \mu\text{g, 0.364 } \mu\text{mol) and ligand 4 (236 } \mu\text{g, 0.364 } \mu\text{mol) in CD}_2\text{Cl}_2 \text{ (0.5 mL) in an NMR tube. The mixture was sonicated for 2-3 min to afford a clear reddish orange solution. }^{1}\text{H NMR analysis of the mixture clearly showed that Cu}^+ \text{ was bound to nanoswitch 1 while ligand 2 and ligand 4 remained free in the solution (see Figures S12 and S13).} \]
Preparation of state II:

Zn(OTf)₂ (171 µg, 0.471 µmol) dissolved in 1.0 mL of CH₃CN was added into the solution of nanoswitch 1 (515 µg, 0.471 µmol) in 9.0 mL of CH₂Cl₂. After stirring for 2-3 min, ligand 2 (299 µg, 0.235 µmol), ligand 4 (153 µg, 0.235 µmol) and [Cu(CH₃CN)₄]PF₆ (176 µg, 0.471 µmol) were added into the same flask. After heating for 30 more min at 60 °C, the solvents were evaporated under reduced pressure and the sample was subjected to ¹H NMR measurement in CD₂Cl₂ without any further purification. Analysis of ¹H NMR confirmed the formation of state II, i.e. 4 × [Zn(1)](OTf)₂ + [Cu₄(2)₄(4)₄](PF₆)₄ (see Figures S14 and S15).

Insitu Switching studies (Fig. S16):

In an NMR tube, nanoswitch 1 (660 µg, 0.604 µmol), ligand 2 (383 µg, 0.302 µmol), ligand 4 (196 µg, 0.302 µmol) and [Cu(CH₃CN)₄]PF₆ (225 µg, 0.604 µmol) were dissolved in 500 µL of CD₂Cl₂. After formation of a clear solution the sample was subjected to NMR measurement (see Figure S16d).

After the measurement, Zn(OTf)₂ (219 µg, 0.604 µmol) dissolved in 200 µL acetonitrile was added to the sample and was subjected to heating at 60 °C for 30 min. The NMR measurement was done for the sample without any further purification (see Figure S16e).

To check the reversibility of the system, finally hexacyclen (156 µg, 0.604 µmol) was added into the same sample that was heated at 60 °C for 10 min (in a thermostat). Thereafter, the sample was cooled to room temperature and the ¹H NMR spectrum was recorded (See Figure S16f).
Assembly and disassembly of Prism P by Nanoswitch 1

In an NMR tube nanoswitch, 1 (568 µg, 0.520 µmol), ligand 3 (241 µg, 0.173 µmol), ligand 4 (168 µg, 0.260 µmol) and [Cu(CH₃CN)₄]PF₆ (194 µg, 0.520 µmol) were dissolved in 500 µL of CD₂Cl₂. The ensuing clear solution was subjected to NMR measurement (see Figure S21d).

After the measurement, Zn(OTf)₂ (189 µg, 0.520 µmol), dissolved in 200 µL acetonitrile, was added to the sample that was subjected to heating at 60 ºC for 30 min. The NMR measurement was taken without any further purification (see Figure S21e).

To check the reversibility of the system, finally hexacyclen (134 µg, 0.520 µmol) was added into the same sample that was heated at 60 ºC for 10 min (in a thermostat). Thereafter, the sample was cooled to room temperature and the ¹H NMR spectrum was recorded (See Figure S21f).

3 ¹H & ¹³C NMR Spectra
Figure S1: $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of compound 2. An expanded part of the aromatic region is shown at the top with characteristic protons assigned.

Figure S2: $^{13}$C NMR spectrum (100 MHz, CD$_2$Cl$_2$, 298 K) of compound 2. An expanded part of the aromatic region is shown at the top.
Figure S3: $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of complex C1 = [Cu(5)(6)]PF$_6$. An expanded part of the aromatic region is shown at the top with characteristic protons assigned.

Figure S4: $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of complex C2 = [Zn(5)(6)](OTf)$_2$. An expanded part of the aromatic region is shown at the top with characteristic protons assigned.
Figure S5: $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of complex C3 = [Cu(5)(7)]PF$_6$. An expanded part of the aromatic region is shown at the top with characteristic protons assigned.

Figure S6: $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of the mixture of ligand 5, 6, 7 and [Cu(CH$_3$CN)$_4$]PF$_6$ in 2:1:1:1 ratio to form complex C1 = [Cu(5)(6)]$^+$ with 1 equiv. of ligand 5 and 7 free in the solution.

Figure S7: $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of mixture of ligand 5, 6, 7, [Cu(CH$_3$CN)$_4$]PF$_6$ and Zn(OTf)$_2$ in 2:1:1:1 ratio to form complex C2 = [Zn(5)(6)]$^{2+}$ and C3 = [Cu(5)(7)]$^+$. 
Figure S8: $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of complex [Cu(I)]PF$_6$. An expanded part of the aromatic region is shown at the top with a few characteristic protons assigned.

Figure S9: $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of complex [Zn(I)](OTf)$_2$. An expanded part of the aromatic region is shown at the top with a few characteristic protons assigned.
Figure S10: $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of 2D rectangle $\mathbf{R} = \text{[Cu}_4(2)_{2}(4)_{2}]^2$(PF$_6$)$_4$. An expanded part of the aromatic region is shown at the top with few characteristic protons assigned.

Figure S11: Partial $^1$H NMR spectra for comparison (400 MHz, CD$_2$Cl$_2$, 298 K) of (a) 2D macrocycle $\mathbf{R} = \text{[Cu}_4(2)_{2}(4)_{2}]^2$+, (b) ligand 2, (c) ligand 4 and (d) prototypical complex $\mathbf{C3} = \text{[Cu}(5)(7)]^+$. 

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Figure S12: $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$, 298 K) of prism $P = [Cu_6(3)_{2}(4)]_3^6$. An expanded part of the aromatic region is shown at the top with characteristic protons assigned.

Figure S13: Partial $^1$H NMR spectra for comparison (400 MHz, CD$_2$Cl$_2$, 298 K) of (a) prism $P = [Cu_6(3)_{2}(4)]_3^6$, (b) ligand 3, (c) ligand 4 and (d) prototypical complex $C3 = [Cu(5)(7)]^+$. 
**Figure S14:** $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of State I = 2 × [Cu(1)]$^+$ + 2 + 4. An expanded part of the aromatic region is shown at the top with characteristic protons assigned.

**Figure S15:** Partial $^1$H NMR spectra for comparison (400 MHz, CD$_2$Cl$_2$, 298 K) of (a) State I, (b) [Cu(1)]$^+$, (c) ligand 2 and (d) ligand 4.
Figure S16: $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of State II = 4 × [Zn(1)]$^{2+}$ + [Cu$_4$(2)$_2$(4)$_2$]$^{4+}$. An expanded part of the aromatic region is shown at the top with characteristic protons assigned.

Figure S17: Partial $^1$H NMR spectra for comparison (400 MHz, CD$_2$Cl$_2$, 298 K) of (a) State II, (b) [Cu$_4$(2)$_2$(4)$_2$]$^{4+}$, (c) [Zn(1)]$^{2+}$. 
Figure S18: $^1$H NMR (400 MHz, 298 K, CD$_2$Cl$_2$) showing the in-situ reversible assembly and disassembly of rectangle R by nanoswitch 1. (a) R = [Cu$_4$(2)(4)$_2$]$_2^+$; (b) [Zn(1)]$^{2+}$; (c) [Cu(1)]$^{+}$; (d) nanoswitch 1, ligand 2, 4 and [Cu(CH$_3$CN)$_4$]PF$_6$ were mixed in 4:2:2:4 ratio affording state I; (e) addition of 4 equiv. Zn(OTf)$_2$ to state I depicted in spectrum (a) generated state II, i.e. [Zn(1)]$^{2+}$ + [Cu$_4$(2)(4)$_2$]$^{4+}$; (f) addition of 4 equiv. of hexacyclen to remove Zn$^{2+}$, regenerated state I along with complex [Zn(hexacyclen)]$^{2+}$. 
Figure S19: $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of State $I' = 6 \times [Cu(1)]^{2+} + 2 \times 3 + 3 \times 4$. An expanded part of the aromatic region is shown at the top with characteristic protons assigned.

Figure S20: Partial $^1$H NMR spectra for comparison (400 MHz, CD$_2$Cl$_2$, 298 K) of (a) State $I'$, (b) [Cu(1)]$^{2+}$, (c) ligand 3 and (d) ligand 4.
Figure S21: $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$, 298 K) of State II’ = 4 × [Zn(1)]$^{2+}$ + [Cu$_6$(3)$_2$(4)$_3$]$^{6+}$. An expanded part of the aromatic region is shown at the top with characteristic protons assigned.
Figure S22: Partial $^1$H NMR spectra for comparison (400 MHz, CD$_2$Cl$_2$, 298 K) of (a) State II', (b) [Cu$_3$(3)$_2$(4)$_3$]$^{6+}$, (c) [Zn(1)]$^{2+}$.

Figure S23: $^1$H NMR (400 MHz, 298 K, CD$_2$Cl$_2$) showing in-situ reversible assembly and disassembly of prism $P$ by nanoswitch 1. (a) $P$= [Cu$_6$(3)$_2$(4)$_3$][PF$_6$]; (b) [Zn(1)]$^{2+}$; (c) [Cu(1)]$^+$; (d) nanoswitch 1, ligand 3, 4 and [Cu(CH$_3$CN)$_4$]PF$_6$ were mixed in 6:2:3:6 ratio affording state I'; (e) addition of 6 equiv. Zn(OTf)$_2$ to state I' depicted in spectrum (a) generated state II', i.e. [Zn(1)]$^{2+}$ + [Cu$_6$(3)$_2$(4)$_3$]$_{8}^{6+}$; (f) addition of 4 equiv. of hexacyclen to remove Zn$^{2+}$, regenerated state I' along with complex [Zn(hexacyclen)]$^{2+}$.
4 ESI-MS spectra

Figure S24: ESI-MS spectrum of 2D rectangle $R = [\text{Cu}_4(\text{2})_2(\text{4})_2](\text{PF}_6)_4$ in CH$_2$Cl$_2$ as well as experimental (black lines) and calculated isotopic distributions (red lines) for the peaks associated with $[\text{Cu}_4(\text{2})_2(\text{4})_2](\text{PF}_6)^{3+}$.

Figure S25: ESI-MS spectrum of prism $P = [\text{Cu}_6(\text{3})_2(\text{4})_2](\text{PF}_6)_6$ in CH$_2$Cl$_2$ as well as experimental (black lines) and calculated isotopic distributions (red lines) for the peak associated with $[\text{Cu}_6(\text{3})_2(\text{4})_2](\text{PF}_6)^{3+}$. 
Figure S26: ESI-MS spectrum of State II, i.e. \([\text{Zn}(1)]^{2+} + \text{Rectangle } \textbf{R} = [\text{Cu}_4(2)_2(4)_2](PF_6)_4\) in CH\(_2\)Cl\(_2\) as well as experimental (black lines) and calculated isotopic distributions (red lines) for the peaks associated with \([\text{Cu}_4(2)_2(4)_2](PF_6)_3^+\) and \([\text{Zn}(1)]^{2+}\).

Figure S27: ESI-MS spectrum of State II’, i.e., \([\text{Zn}(1)]^{2+} + \text{Prism } \textbf{P} = [\text{Cu}_6(3)_2(4)_3](PF_6)_6\) in CH\(_2\)Cl\(_2\).
5 UV-vis Data

Figure S28. UV-vis spectra of complexes [Cu(1)]\(^+\) and [Zn(1)]\(^{2+}\) in CH\(_2\)Cl\(_2\) (10\(^{-5}\) M) at 298 K.

Figure S29. UV-vis spectra taken during the kinetic study of [Cu(1)]\(^+\) upon addition of Zn(OTf)\(_2\) to afford [Zn(1)]\(^{2+}\) in CH\(_2\)Cl\(_2\) (10\(^{-5}\) M) at 298 K.
**Figure S30.** UV-vis spectra taken during the kinetic study (at $1 \times 10^{-5}$ M) of ([Cu(1)]$^{+2+4}$) (State I) upon addition of Zn(OTf)$_2$ to furnish ([Zn(1)]$^{2+}$ + R) in CH$_2$Cl$_2$ at 298 K.

**Figure S31.** UV-vis spectra taken during the kinetic study of ([Zn(1)]$^{2+}$ + R) (State II) upon addition of hexacyclen to furnish ([Cu(1)]$^{+2+4}$) (State I) in CH$_2$Cl$_2$ (at $1 \times 10^{-5}$ M) at 298 K.
**5 DOSY NMR**

**Figure S32:** DOSY-NMR spectrum (600 MHz, CD$_2$Cl$_2$, 298 K) of rectangle $\text{R} = [\text{Cu}_4(2)_{2}(4)_{2}](\text{PF}_6)_4$ showing a single diffusion coefficient: $D = 4.6 \times 10^{-10}$ m$^2$ s$^{-1}$.

**References**