Electronic Supplementary Information

Selective and Reversible Interconversion of Nanosliders Commanded by Remote Control via Metal Ion Signaling

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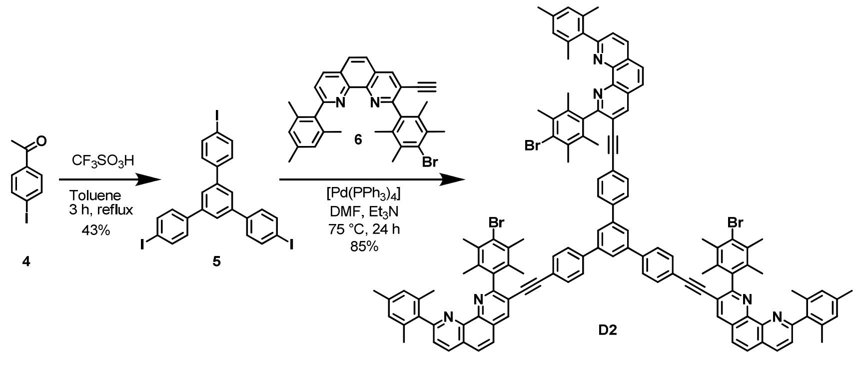
1. Synthesis

1.1 General Information

All solvents were dried by distillation prior to use while commercial reagents were used without any further purification. Bruker Avance (400 MHz) and Varian (600 MHz) spectrometers were used to measure ^{1}H and ^{13}C NMR spectra using a deuterated solvent as the lock and residual protiated solvent as internal reference ($CDCl_3$: δ_H 7.26 ppm, δ_C 77.0 ppm; CD_2Cl_2: δ_H 5.32 ppm, δ_C 53.8 ppm). The following abbreviations were used to define NMR peak pattern: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublets of doublets, dt = doublet of triplets, td = triplet of doublets, brs = broad signal, m = multiplet. The coupling constant values are given in Hertz (Hz). Wherever possible, assignments of protons are done. The numbering of different carbons in different molecular skeletons was not necessarily done following the IUPAC nomenclature rules; it is exclusively done for assigning NMR signals. All electrospray ionization (ESI-MS) spectra were recorded on a Thermo-Quest LCQ deca and the theoretical isotopic distributions of the mass signals were calculated (https://omics.pnl.gov/software/molecular-weight-calculator). Melting points were measured on a BÜCHI 510 instrument and are not corrected. Infrared spectra were recorded on a Perkin Elmer Spectrum-Two FT-IR spectrometer. Elemental analysis was performed using the EA-3000 CHNS analyzer. UV-vis spectra were recorded on a Varian Cary 100 BioUV/Vis spectrometer. Column chromatography was performed either on silica gel (60-400 mesh) or neutral alumina (Fluka, 0.05-0.15 mm, Brockmann Activity 1). Merck silica gel (60 F254) or neutral alumina (150 F254) sheets were used for thin layer chromatography (TLC). Preparations of metal complexes were performed directly in the NMR tube using CD_2Cl_2 as solvent.

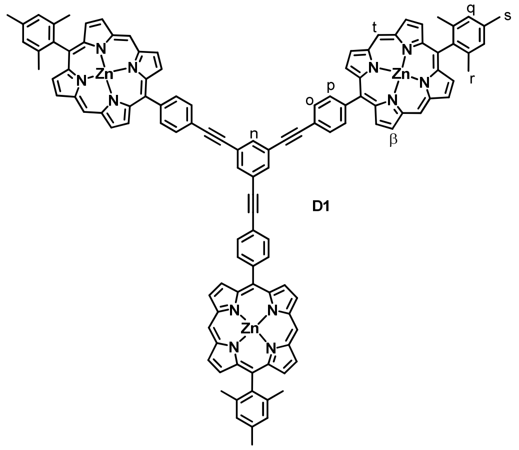
1.2 Synthesis and Characterization of Ligands



Scheme S1. Reaction scheme to prepare the deck **D2**.

Synthesis of **5**[1] and **6**[2] was accomplished by literature known procedures.

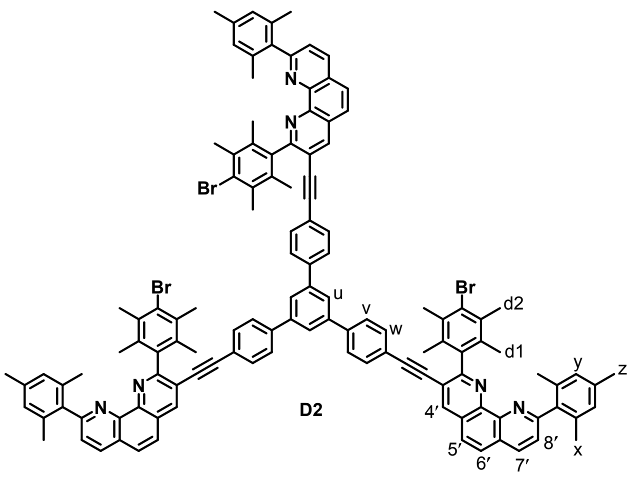
1.2.1 Synthesis of Deck **D1**[3]



Synthesis of deck **D1** was performed along a literature-known procedure.[3]

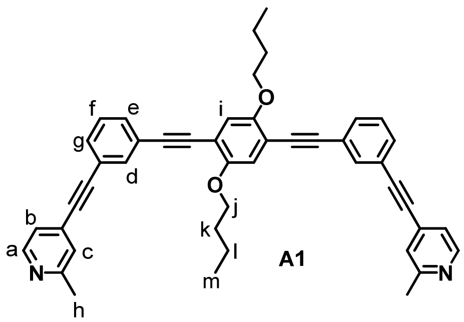
^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 1.83 (s, 18H, r-H), 2.67 (s, 9H, s-H), 7.36 (s, 6H, q-H), 8.14 (s, 3H, n-H), 8.15 (d, ^3J = 8.4 Hz, 6H, o-H), 8.39 (d, ^3J = 8.4 Hz, 6H, p-H), 8.98 (d, ^3J = 4.4 Hz, 6H, β-H), 9.23 (d, ^3J = 4.4 Hz, 6H, β-H), 9.46 (d, ^3J = 4.4 Hz, 6H, β-H), 9.54 (d, ^3J = 4.4 Hz, 6H, β-H), 10.36 (s, 6H, t-H) ppm.

1.2.2 Synthesis of Deck **D2**



Compounds **5** (60.0 mg, 87.7 μmol) and **6** (187 mg, 351 μmol) were dissolved in dry DMF (15 mL) and dry Et_3N (15 mL) in a sealed tube under N_2 atmosphere. The mixture was degassed by using two freeze-pump-thaw cycles. Then $Pd(PPh_3)_4$ (15.0 mg, 13.0 μmol) was added under N_2 atmosphere. After further degassing by freeze-pump-thaw cycles, the reaction mixture was stirred at 85 ºC for 16 h. The solvent was evaporated under reduced pressure. The residue was poured on ice cold water to dissolve DMF in the aqueous layer. The organic part was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and concentrated. The compound was purified by gel column chromatography (SiO_2) using 40% EtOAc in hexane as eluent to afford a colorless solid (142 mg, 85%). $\boldsymbol{R_f}$ = 0.3 (SiO_2, 40% EtOAc in hexane). **mp:** > 200 ºC. **IR (KBr):** ν = 596.4, 639.0, 695.1, 720.6, 759.0, 770.7, 811.9, 829.2, 847.7, 896.3, 911.1, 985.6, 1017.0, 1060.8, 1100.1, 1127.1, 1140.7, 1160.2, 1262.6, 1295.1, 1384.1, 1417.0, 1438.9, 1457.5, 1481.4, 1504.0, 1533.9, 1584.0, 1599.9, 1613.9, 2205.4, 2856.8, 2918.6, 2952.5 cm^{-1}. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 2.04 (s, 18H, d2-H), 2.11 (s, 18H, x-H), 2.31 (s, 9H, z-H), 2.47 (s, 18H, d1-H), 6.93 (s, 6H, y-H), 7.21 (d, ^3J = 8.0 Hz, 6H, v-H), 7.58-7.62 (m, 9H, w-H + 8'-H), 7.73 (s, 3H, u-H), 7.86 (d, ^3J = 8.0 Hz, 3H, 6'-H), 7.90 (d, ^3J = 8.0 Hz, 3H, 5'-H), 8.30 (d, ^3J = 8.0 Hz, 3H, 7'-H), 8.51 (s, 3H, 4'-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 18.6, 20.5, 21.0, 21.1, 87.8, 95.3, 120.1, 122.0, 125.2, 125.6, 126.9 (2C), 127.1, 127.3, 127.6, 128.5, 129.2, 132.0 (2C), 133.6, 135.9, 136.0, 137.6, 137.8, 138.3, 139.1, 140.9, 141.6, 144.7, 145.8, 160.6, 162.5 ppm. **Elemental analysis:** Anal. Calcd for $C_{123}H_{99}Br_3N_6$•0.8 CH_2Cl_2: C, 75.52; H, 5.15; N, 4.27. Found: C, 75.92; H, 4.72; N, 4.19. **ESI-MS:** *m/z* (%) 951.6 (100) $[M + 2H]^{2+}$, 1901.5 (40) $[M + H]^{+}$, 634.8 (15) $[M + 3H]^{3+}$.

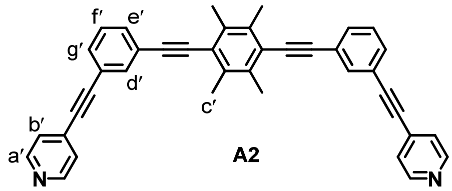
1.2.3 Characterization of Biped **A1**[4]



Synthesis of biped **A1** was accomplished using the literature-known procedure.4

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 1.03 (t, ^3J = 7.4 Hz, 6H, m-H), 1.57-1.64 (m, 4H, l-H), 1.82-1.88 (m, 4H, k-H), 2.54 (s, 6H, h-H), 4.06 (t, ^3J = 6.4 Hz, 4H, j-H), 7.05 (s, 2H, i-H), 7.21 (dd, ^3J = 5.2 Hz, ^4J = 1.2 Hz, 2H, b-H), 7.28 (brs, 2H, c-H), 7.40 (t, ^3J = 7.8 Hz, 2H, f-H), 7.53-7.56 (m, 4H, e-H+g-H), 7.71-7.72 (m, 2H, d-H), 8.48 (dd, ^3J = 5.2 Hz, ^4J = 0.6 Hz, 2H, a-H) ppm.

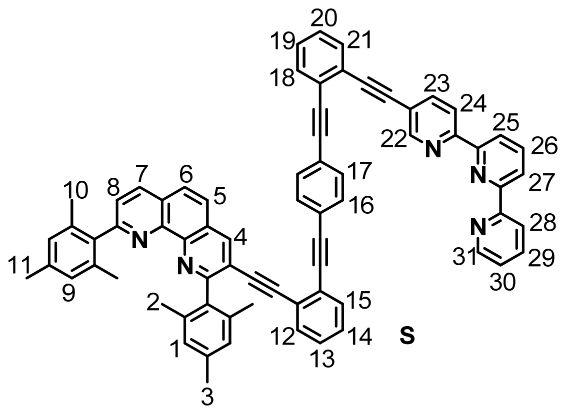
1.2.4 Characterization of Biped **A2**[3]



Synthesis of biped **A2** was accomplished using the literature-known procedure.[3]

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.53 (s, 12H, c'-H), 7.41 (d, ^3J = 6.0 Hz, 4H, b'-H), 7.43 (td, ^3J = 8.0 Hz, ^5J = 0.4 Hz, 2H, f'-H), 7.55 (dt, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 2H, e'-H), 7.60 (dt, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 2H, g'-H), 7.77 (td, ^4J = 1.6 Hz, ^5J = 0.4 Hz, 2H, d'-H),8.60 (d, ^3J = 6.0 Hz, 4H, a'-H) ppm.

1.2.5 Characterization of Switch **S**:

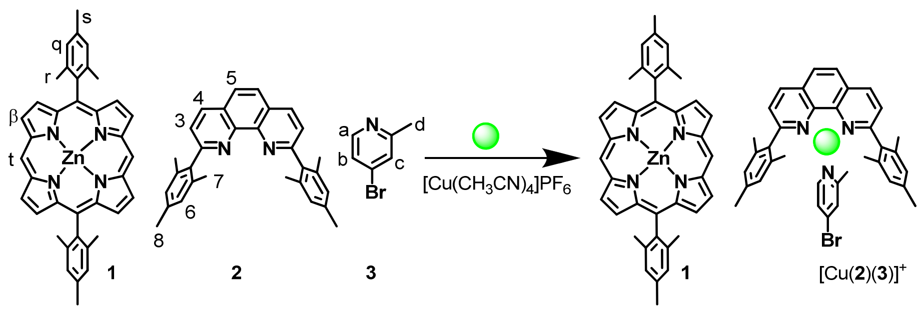


The synthesis of switch **S** will be given in a separate publication. Here we provide relevant ^{1}H NMR data for comparison with those of the complexes.

mp: > 200 ºC. **IR (KBr):** ν = 758.7, 787.4, 848.7, 887.2, 991.7, 1019.1, 1102.9, 1147.8, 1261.1, 1429.5, 1452.4, 1475.2, 1511.6, 1582.7, 1614.7, 2856.0, 2945.9, 3058.0 cm^{-1}. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 2.01 (s, 6H, 10-H), 2.05 (s, 6H, 2-H), 2.32 (s, 3H, 11-H), 2.35 (s, 3H, 3-H), 6.93 (s, 2H, 9-H), 6.95 (s, 2H, 1-H), 7.00 (dd, ^3J = 7.8 Hz, ^4J = 1.0 Hz, 1H, 12-H), 7.23-7.34 (m, 3H, 13-H+14-H+30-H), 7.39-7.46 (m, 2H, 19-H+21-H), 7.49 (d, ^3J = 8.0 Hz, 1H, 8-H), 7.54 (dd, ^3J = 7.8 Hz, ^4J = 1.0 Hz, 1H, 15-H), 7.63-7.70 (m, 6H, 16-H+17-H+18-H+20-H), 7.74-7.79 (m, 3H, 29-H+5-H+6-H), 7.89 (dd, ^3J = 7.8 Hz, ^3J = 7.8 Hz, 1H, 26-H), 8.06 (dd, ^3J = 8.2 Hz, ^4J = 2.0 Hz, 1H, 23-H), 8.19 (d, ^3J = 8.0 Hz, 1H, 7-H), 8.41-8.45 (m, 2H, 25-H+27-H), 8.51 (s, 1H, 4-H), 8.53-8.55 (m, 1H, 28-H), 8.64 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.8 Hz, 1H, 31-H), 8.68 (dd, ^3J = 8.2 Hz, ^5J = 0.8 Hz, 1H, 24-H), 8.91 (dd, ^4J = 2.0 Hz, ^5J = 0.8 Hz, 1H, 22-H) ppm. **ESI-MS:** *m/z* (%) 972.8 (100) [**S** + H]$^+$.

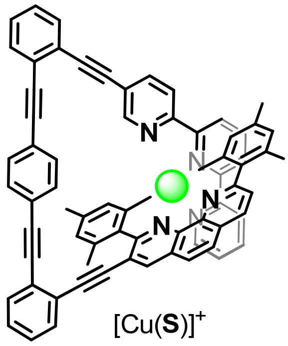
1.3 Synthesis and Characterization of Complexes

1.3.1 Model Complex



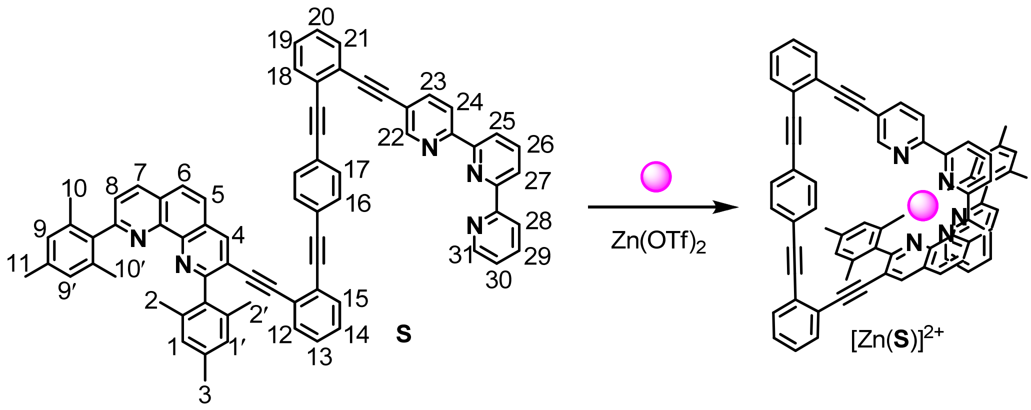
In an NMR tube, compounds **1** (0.917 mg, 1.50 µmol), **2** (0.626 mg, 1.50 µmol), **3** (0.259 mg, 1.50 µmol) and $[Cu(CH_3CN)_4]PF_6$ (0.560 mg, 1.50 µmol) were dissolved in CD_2Cl_2 to furnish complex [Cu(**2**)(**3**)]$^+$ along with free **1**. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 1.81 (s, 15H, r-H+d-H), 1.99 (s, 12H, 7-H), 2.16 (s, 6H, 8-H), 2.66 (s, 6H, s-H), 6.76 (s, 4H, 6-H), 7.10 (dd, ^3J = 5.8 Hz, ^4J = 1.4 Hz, 1H, b-H), 7.18 (d, ^3J = 1.4 Hz, 1H, c-H), 7.21 (d, ^3J = 5.8 Hz, 1H, a-H), 7.34 (s, 4H, q-H), 7.93 (d, ^3J = 8.2 Hz, 2H, 3-H), 8.18 (s, 2H, 5-H), 8.71 (d, ^3J = 8.2 Hz, 2H, 4-H), 8.93 (d, ^3J = 4.6 Hz, 4H, β-H), 9.41 (d, ^3J = 4.6 Hz, 4H, β-H), 10.26 (s, t-H) ppm.

1.3.2 Preparation of Complex $[Cu(\mathbf{S})]^+$



In an NMR tube, switch **S** (1.50 mg, 1.54 μmol) and $[Cu(CH_3CN)_4]PF_6$ (0.575 mg, 1.54 μmol) were dissolved in 600 μL of CD_2Cl_2 to furnished complex $[Cu(\mathbf{S})]^+$ in quantitative yield. **IR (KBr):** ν = 557.2, 587.4, 610.0, 633.1, 666.1, 695.7, 722.2, 755.2, 781.6, 843.3, 868.7, 897.5, 923.4, 953.1, 986.1, 1015.8, 1039.0, 1042.2, 1073.0, 1105.0, 1121.4, 1164.1, 1200.0, 1240.2, 1263.3, 1299.6, 1329.3, 1384.4, 1451.3, 1510.7, 1603.0, 1636.3, 1703.2, 1725.2, 2223.4, 2856.6, 2922.8, 2952.5 cm^{-1}. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 1.32 (s, 3H, 2-H), 1.49 (s, 3H, 10-H), 1.79 (s, 6H, 10'-H+2'-H), 1.92 (s, 3H, 3-H), 1.99 (s, 3H, 11-H), 6.12 (s, 1H, 9-H), 6.23 (s, 1H, 9'-H), 6.34 (s, 1H, 1-H), 6.38 (s, 1H, 1'-H), 7.21-7.26 (m, 2H, 15-H+18-H), 7.27-7.31 (m, 3H, 14-H+19-H+29-H), 7.32-7.38 (m, 3H, 24-H+26-H+30-H), 7.39-7.43 (m, 4H, 16-H+17-H), 7.44-7.49 (m, 2H, 13-H+20-H), 7.56-7.61 (m, 2H, 12-H+21-H), 7.69 (d, ^3J = 8.2 Hz, 1H, 28-H), 7.76 (d, ^3J = 8.2 Hz, 1H, 8-H), 7.78 (d, ^3J = 8.2 Hz, 1H, 6-H), 7.88-7.94 (m, 3H, 22-H+25-H+27-H), 8.02-8.08 (m, 2H, 31-H+23-H), 8.12 (d, ^3J = 8.2 Hz, 1H, 5-H), 8.51 (s, 1H, 4-H), 8.56 (d, ^3J = 8.2 Hz, 1H, 7-H) ppm. **Elemental analysis:** Anal. Calcd for $C_{71}H_{49}CuF_6N_5P{\bullet}2CH_2Cl_2$: C, 64.92; H, 3.96; N, 5.19. Found: C, 65.22; H, 3.78; N, 4.80. **ESI-MS:** *m/z* (%) 1034.9 (100) $[Cu(\mathbf{S})]^+$.

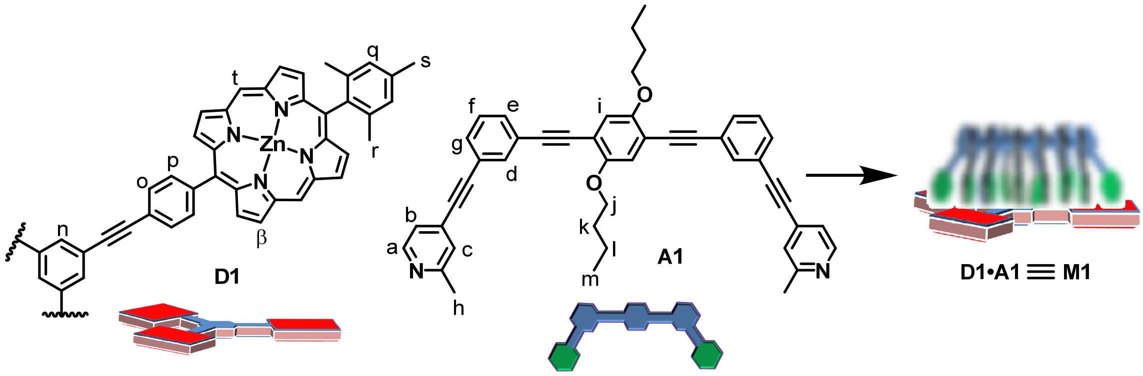
1.3.3 Preparation of Complex $[Zn(\mathbf{S})]^{2+}$



In an NMR tube, switch **S** (1.50 mg, 1.54 µmol) was dissolved in proper amount of CD_2Cl_2. $Zn(OTf)_2$ (0.560 mg, 1.54 µmol) was added subsequently as a standard solution in CD_3CN. After sonication for 2-3 min $[Zn(\mathbf{S})]^{2+}$ was afforded in quantitative manner. **IR (KBr):** ν = 501.1, 523.9, 560.5, 573.7, 610.0, 639.3, 668.4, 702.3, 761.8, 785.3, 804.7, 824.5, 847.6, 867.4, 1033.0, 1065.3, 1108.2, 1161.0, 1230.3, 1259.9, 1385.3, 1451.3, 1484.3, 1510.7, 1563.5, 1632.8, 2853.5, 2922.8, 2959.0 cm^{-1}. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 0.84 (s, 3H, 10-H), 1.08 (s, 3H, 2-H), 1.22 (s, 3H, 10'-H), 1.35 (s, 3H, 2'-H), 1.74 (s, 3H, 11-H), 1.82 (s, 3H, 3-H), 6.06 (s, 1H, 9-H), 6.17 (s, 1H, 1-H), 6.19 (s, 1H, 9'-H), 6.26 (s, 1H, 1'-H), 7.15 (d, ^3J = 8.0 Hz, 2H, 16/17-H), 7.27 (d, ^3J = 8.0 Hz, 2H, 17/16-H), 7.30-7.45 (m, 6H, 13-H+14-H+15-H+18-H+19-H+20-H), 7.49-7.52 (m, 1H, 21/12-H), 7.58-7.60 (m, 2H, 30-H+12/21-H), 7.75 (d, ^3J = 4.6 Hz, 1H, 31-H), 7.83 (dd, ^4J = 2.0 Hz, ^5J = 0.6 Hz, 1H, 22-H), 8.09 (d, ^3J = 8.4 Hz, 1H, 8-H), 8.26 (td, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1H, 29-H), 8.41 (dd, ^3J = 8.4 Hz, ^4J = 2.0 Hz, 1H, 23-H), 8.45 (d, ^3J = 9.2 Hz, 1H, 6-H), 8.47-8.51 (m, 2H, 27-H+28-H), 8.55 (dd, ^3J = 8.0 Hz, ^3J = 8.0 Hz, 1H, 26-H), 8.56 (d, ^3J = 9.2 Hz, 1H, 5-H), 8.60 (dd, ^3J = 8.0 Hz, ^4J = 1.0 Hz, 1H, 25-H), 8.65 (dd, ^3J = 8.4 Hz, ^5J = 0.6 Hz, 1H, 24-H), 9.09 (d, ^3J = 8.4 Hz, 1H, 7-H), 9.21 (s, 1H, 4-H) ppm. **Elemental analysis:** Anal.

Calcd for $C_{73}H_{49}F_6N_5O_6S_2Zn{\bullet}5\ CH_2Cl_2$: C, 53.22; H, 3.38; N, 3.98; S, 3.64. Found: C, 53.31; H, 3.13; N, 3.73; S, 3.41. **ESI-MS:** *m/z* (%) 518.6 (100) $[Zn(\mathbf{S})]^{2+}$.

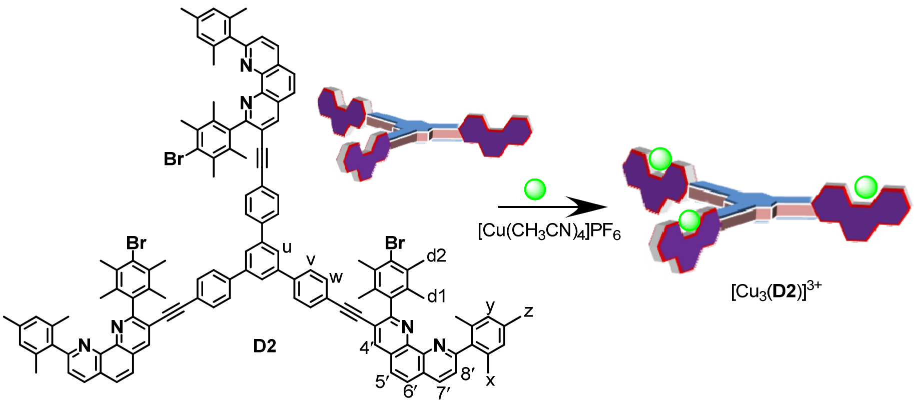
1.3.4 Characterization of Nanoslider **D1•A1** (=**M1**)[5]



Nanoslider **D1•A1** (**M1**) was synthesized by the literature known procedure.[5]

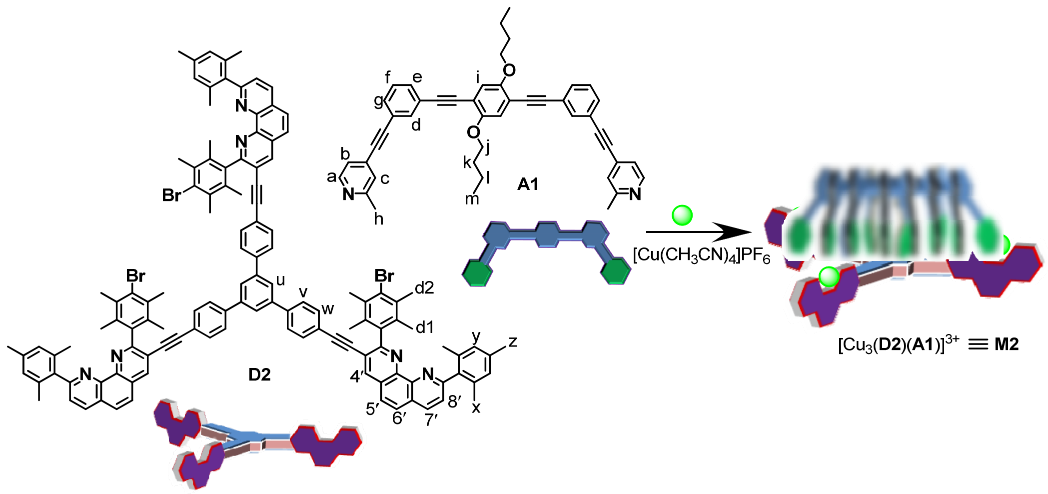
^{1}H NMR (CD_2Cl_2, 400 MHz): δ = −0.24 (brs, 6H, h-H), 0.90 (t, ^3J = 7.4 Hz, 6H, m-H), 1.43-1.52 (m, 4H, l-H), 1.69-1.76 (m, 4H, k-H), 1.83 (s, 18H, r-H), 2.67 (s, 9H, s-H), 3.93 (t, ^3J = 6.4 Hz, 4H, j-H), 4.11 (brs, 2H, a-H), 6.00 (brs, 2H, b-H), 6.08 (brs, 2H, c-H), 6.91 (s, 2H, i-H), 7.21-7.22 (m, 4H, e-H+f-H), 7.35 (s, 6H, q-H), 7.38-7.40 (m, 4H, d-H+g-H), 8.13-8.15 (m, 9H, o-H+n-H), 8.38 (d, ^3J = 8.0 Hz, 6H, p-H), 8.94 (d, ^3J = 4.6 Hz, 6H, β-H), 9.19 (d, ^3J = 4.6 Hz, 6H, β-H), 9.41 (d, ^3J = 4.6 Hz, 6H, β-H), 9.49 (d, ^3J = 4.6 Hz, 6H, β-H), 10.29 (s, 6H, t-H) ppm.

1.3.5 Preparation of Complex $[Cu_3(\mathbf{D2})]^{3+}$



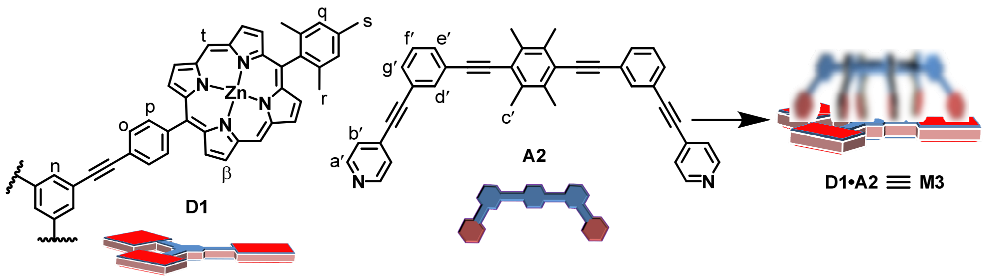
In an NMR tube, deck **D2** (1.40 mg, 0.736 μmol), and 3.0 equiv of $[Cu(CH_3CN)_4]PF_6$ (0.824 mg, 2.21 μmol) were dissolved in 550 μL of CD_2Cl_2 to afford $[Cu_3(\mathbf{D2})]^{3+}$ in quantitative yield. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 2.04 (s, 18H, d2-H), 2.05 (s, 18H, x-H), 2.36 (s, 9H, z-H), 2.53 (s, 18H, d1-H), 7.02 (s, 6H, y-H), 7.30 (d, ^3J = 8.2 Hz, 6H, v-H), 7.69 (d, ^3J = 8.2 Hz, 6H, w-H), 7.80 (s, 3H, u-H), 7.91 (d, ^3J = 8.2 Hz, 3H, 8'-H), 8.15 (d, ^3J = 9.0 Hz, 3H, 6'-H), 8.18 (d, ^3J = 9.0 Hz, 3H, 5'-H), 8.68 (d, ^3J = 8.2 Hz, 3H, 7'-H), 8.84 (s, 2H, 4'-H) ppm. **ESI-MS:** *m/z* (%) 702.7 (100) $[Cu_3(\mathbf{D2})(H_2O)]^{3+}$.

1.3.6 Preparation of Nanoslider $[Cu_3(\mathbf{D2})(\mathbf{A1})]^{3+}$ (=**M2**)



In an NMR tube, deck **D2** (1.40 mg, 0.736 µmol), biped **A1** (0.481 mg, 0.736 µmol), and 3.0 equiv of $[Cu(CH_3CN)_4]PF_6$ (0.824 mg, 2.21 µmol) were dissolved in 550 µL of CD_2Cl_2 to obtain $[Cu_3(\mathbf{D2})(\mathbf{A1})]^{3+}$ in quantitative yield. **IR (KBr):** ν = 562.8, 634.2, 685.5, 732.9, 848.4, 990.2, 1021.9, 1065.4, 1089.2, 1113.0, 1164.4, 1223.7, 1279.1, 1384.3, 1425.6, 1441.4, 1465.1, 1469.0, 1504.7, 1552.2, 1615.5, 1742.2, 2217.0, 2854.3, 2293.2, 2942.2 cm^{-1}. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 1.05 (t, ^3J = 7.4 Hz, 6H, m-H), 1.59-1.67 (m, 4H, l-H), 1.85-1.91 (m, 10H, k-H +h-H), 2.02 (s, 18H, d2-H), 2.04 (s, 18H, x-H), 2.23 (s, 9H, z-H), 2.37 (s, 18H, d1-H), 4.08 (t, ^3J = 6.4 Hz, 4H, j-H), 6.87 (s, 6H, y-H), 7.09-7.11 (m, 4H, i-H+b-H), 7.17 (s, 2H, c-H), 7.31 (d, ^3J = 8.2 Hz, 6H, v-H), 7.43-7.48 (m, 2H, f-H), 7.54 (brs, 2H, a-H), 7.56-7.60 (m, 4H, e-H+g-H), 7.65 (d, ^3J = 8.2 Hz, 6H, w-H), 7.75 (s, 3H, u-H), 7.79 (s, 2H, d-H), 7.95 (d, ^3J = 8.2 Hz, 3H, 8'-H), 8.18 (d, ^3J = 9.0 Hz, 3H, 6'-H), 8.21 (d, ^3J = 9.0 Hz, 3H, 5'-H), 8.72 (d, ^3J = 8.2 Hz, 3H, 7'-H), 8.87 (s, 2H, 4'-H) ppm. **Elemental analysis:** Anal. Calcd for $C_{169}H_{139}N_8Br_3Cu_3F_{18}O_2P_3$•0.10 CH_2Cl_2: C, 63.71; H, 4.40; N, 3.52. Found: C, 63.33; H, 4.20; N, 3.23. **ESI-MS:** *m/z* (%) 915.2 (100) $[Cu_3(\mathbf{D2})(\mathbf{A1})]^{3+}$.

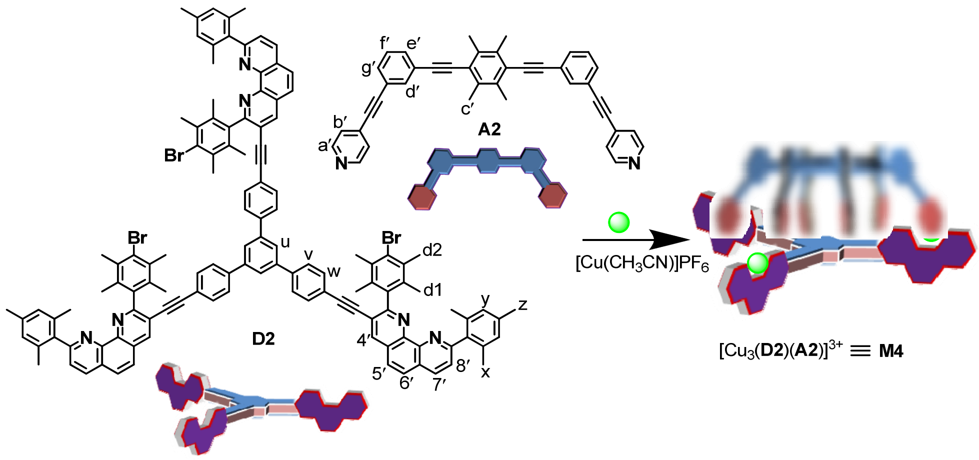
1.3.7 Characterization of Nanoslider **D1•A2** (=**M3**)[5]



Nanoslider **D1•A2** (**M3**) was synthesized along the literature known procedure.[5]

^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 1.84 (s, 18H, r-H), 2.23 (brs, 4H, a'-H), 2.30 (s, 12H, c'-H), 2.67 (s, 9H, s-H), 5.45 (brs, 4H, b'-H), 6.99 (d, ^3J = 7.8 Hz, 2H, e'-H), 7.12 (t, ^3J = 7.8 Hz, 2H, f'-H), 7.23 (s, 2H, d'-H), 7.33 (d, ^3J = 7.8 Hz, 2H, g'-H), 7.36 (s, 6H, q-H), 8.14 (d, ^3J = 8.0 Hz, 6H, o-H), 8.16 (s, 3H, n-H), 8.39 (d, ^3J = 8.0 Hz, 6H, p-H), 8.93 (d, ^3J = 4.4 Hz, 6H, β-H), 9.19 (d, ^3J = 4.4 Hz, 6H, β-H), 9.39 (d, ^3J = 4.4 Hz, 6H, β-H), 9.47 (d, ^3J = 4.4 Hz, 6H, β-H), 10.25 (s, 6H, t-H) ppm.

1.3.8 Preparation of Nanoslider $[Cu_3(\mathbf{D2})(\mathbf{A2})]^{3+}$ (=**M4**):



In an NMR tube, deck **D2** (1.40 mg, 0.736 μmol), biped **A2** (0.395 mg, 0.736 μmol), and 3.0 equiv. of $[Cu(CH_3CN)_4]PF_6$ (0.824 mg, 2.21 μmol) were dissolved in 550 μL of CD_2Cl_2 to obtain $[Cu_3(\mathbf{D2})(\mathbf{A2})]^{3+}$ in quantitative yield. **IR (KBr):** ν = 559.7, 639.3, 693.8, 734.8, 849.2, 990.5, 1017.8, 1034.8, 1072.4, 1108.9, 1130.3, 1161.0, 1266.7, 1384.4, 1423.6, 1437.2, 1461.1, 1502.5, 1560.0, 1607.1, 1638.3, 2210.9, 2323.9, 2852.5, 2924.9 cm^{-1}. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 2.10 (s, 36H, d2-H+x-H), 2.39 (s, 9H, z-H), 2.49 (s, 12H, c'-H), 2.57 (s, 18H, d1-H), 6.58 (brs, 4H, a'-H), 7.02 (s, 6H, y-H), 7.14 (d, ^3J = 6.2 Hz, 4H, b'-H), 7.33 (d, ^3J = 8.2 Hz, 6H, v-H), 7.47 (t, ^3J = 8.0 Hz, 2H, f'-H), 7.58 (d, ^3J = 8.0 Hz, 2H, e'-H), 7.64 (d, ^3J = 8.0 Hz, 2H, g'-H), 7.69 (d, ^3J = 8.2 Hz, 6H, w-H), 7.80 (s, 3H, u-H), 7.87 (s, 2H, d'-H), 7.94 (d, ^3J = 8.2 Hz, 3H, 8'-H), 8.18 (d, ^3J = 9.0 Hz, 3H, 6'-H), 8.22 (d, ^3J = 9.0 Hz, 3H, 5'-H), 8.72 (d, ^3J = 8.2 Hz, 3H, 7'-H), 8.89 (s, 3H, 4'-H) ppm. **Elemental analysis:** Anal. Calcd for $C_{163}H_{127}N_8Br_3Cu_3F_{18}P_3$• CH_2Cl_2: C, 62.57; H, 4.13; N, 3.56. Found: C, 62.88; H, 3.82; N, 3.74. **ESI-MS:** *m/z* (%) 877.2 (100) $[Cu_3(\mathbf{D2})(\mathbf{A2})]^{3+}$.

1.4 Preparation of NetStates

1.4.1 Fabrication of NetState-I ($[Cu(\mathbf{S})]^+$, **M1** and free deck **D2**)

In an NMR tube, decks **D1** (1.10 mg, 0.595 µmol), **D2** (1.13 mg, 0.595 µmol), biped **A1** (0.388 mg, 0.595 µmol), switch **S** (1.74 mg, 1.78 µmol) and $[Cu(CH_3CN)_4]PF_6$ (0.663 mg, 1.78 µmol) were dissolved in 550 µL of CD_2Cl_2 to obtain NetState-I. It was characterized by comparison ^1H NMR with $[Cu(\mathbf{S})]^+$, **M1** and **D2**.

1.4.2 Fabrication of NetState-II ($[Zn(\mathbf{S})]^{2+}$, **M2** and free deck **D1**)

In an NMR tube, decks **D1** (1.10 mg, 0.595 µmol), **D2** (1.13 mg, 0.595 µmol), biped **A1** (0.388 mg, 0.595 µmol), switch **S** (1.74 mg, 1.78 µmol), $[Cu(CH_3CN)_4]PF_6$ (0.663 mg, 1.78 µmol) and $Zn(OTf)_2$ (0.651 mg, 1.78 µmol) as a standard solution in CD_3CN were dissolved in 550 µL of CD_2Cl_2. It was sonicated for 1 h. Then the solvent was evaporated to get rid of CD_3CN. Redissolving it again in CD_2Cl_2 fabricate NetState-II quantitatively. It was characterized by comparison ^1H NMR with $[Zn(\mathbf{S})]^{2+}$, **M2** and **D1**.

1.4.3 Switching between NetState-I and NetState-II

At first switch **S** (1.74 mg, 1.78 µmol), decks **D1** (1.10 mg, 0.595 µmol), **D2** (1.13 mg, 0.595 µmol), biped **A1** (0.388 mg, 0.595 µmol), and $[Cu(CH_3CN)_4]PF_6$ (0.663 mg, 1.78 µmol) were dissolved in 550 µL of CD_2Cl_2 in an NMR tube to furnish NetState-I.

Now to the same NMR tube 3.0 equiv of $Zn(OTf)_2$ (0.651 mg, 1.78 µmol) as a standard solution in CD_3CN were added and sonicated for 1 h. The solvent was evaporated to get rid of CD_3CN. Dissolving it again in CD_2Cl_2 showed formation of NetState-II.

Now to refurnish NetState-I, 3.0 equiv of hexacyclen (0.462 mg, 1.78 µmol) was added to the same NMR tube and sonicated for 15 min.

Three more equiv of $Zn(OTf)_2$ (0.651 mg, 1.78 μmol) as a standard solution in CD_3CN were added and sonicated for 1 h. Evaporation of solvent and dissolution in CD_2Cl_2 showed formation of NetState-II.

Finally addition of 3.0 equiv of hexacyclen (0.462 mg, 1.78 μmol) to the system followed by sonication for 15 min completed the two cycles by regenerating NetState-I.

After each step ^1H NMR was measured.

1.4.4 Fabrication of NetState-III ($[Cu(\mathbf{S})]^+$, **M1**, **M3** and free deck **D2**)

In an NMR tube, switch **S** (1.43 mg, 1.48 μmol), decks **D1** (1.82 mg, 0.984 μmol), **D2** (0.936 mg, 0.492 μmol), bipeds **A1** (0.321 mg, 0.492 μmol), **A2** (0.264 mg, 0.492 μmol) and $[Cu(CH_3CN)_4]PF_6$ (0.550 mg, 1.48 μmol) were dissolved in 550 μL of CD_2Cl_2 to obtain NetState-III.

1.4.5 Fabrication of NetState-IV (3 × $[Zn(\mathbf{S})]^{2+}$, **M2**, **D1** and **D1•A2**)

In an NMR tube, switch **S** (1.43 mg, 1.48 μmol), decks **D1** (1.82 mg, 0.984 μmol), **D2** (0.936 mg, 0.492 μmol), bipeds **A1** (0.321 mg, 0.492 μmol), **A2** (0.264 mg, 0.492 μmol), $[Cu(CH_3CN)_4]PF_6$ (0.550 mg, 1.48 μmol) and $Zn(OTf)_2$ (0.536 mg, 1.48 μmol; as a standard solution in CD_3CN) were dissolved in 550 μL of CD_2Cl_2. It was sonicated for 1 h. Then the solvent was evaporated to get rid of CD_3CN. Redissolving it again in CD_2Cl_2 demonstrated quantitative formation of NetState-IV.

1.4.6 Switching between NetState-III and NetState-IV

At first, switch **S** (1.43 mg, 1.48 μmol), decks **D1** (1.82 mg, 0.984 μmol), **D2** (0.936 mg, 0.492 μmol), bipeds **A1** (0.321 mg, 0.492 μmol), **A2** (0.264 mg, 0.492 μmol) and $[Cu(CH_3CN)_4]PF_6$ (0.550 mg, 1.48 μmol) were dissolved in 550 μL of CD_2Cl_2 in an NMR tube to furnish NetState-III.

To this mixture, 3.0 equiv of $Zn(OTf)_2$ (0.536 mg, 1.48 µmol; as a standard solution in CD_3CN) were added and sonicated for 1 h. The solvent was evaporated to get rid of CD_3CN. Dissolving it again in CD_2Cl_2 showed formation of NetState-IV.

To refurnish NetState-III, 3.0 equiv of hexacyclen (0.382 mg, 1.48 µmol) were added to the above mixture and sonicated for 15 min.

Three more equiv of $Zn(OTf)_2$ (0.536 mg, 1.48 µmol; as a standard solution in CD_3CN) were added and sonicated for 1 h. Evaporation of solvent and dissolving it again in CD_2Cl_2 showed formation of NetState-IV.

Finally addition of 3.0 equiv of hexacyclen (0.382 mg, 1.48 µmol) to the system followed by sonication for 15 min completed the second cycle by regenerating NetState-III.

After each step ^1H NMR was measured.

2. NMR Spectra: ^1H, ^{13}C, ^1H-^1H COSY

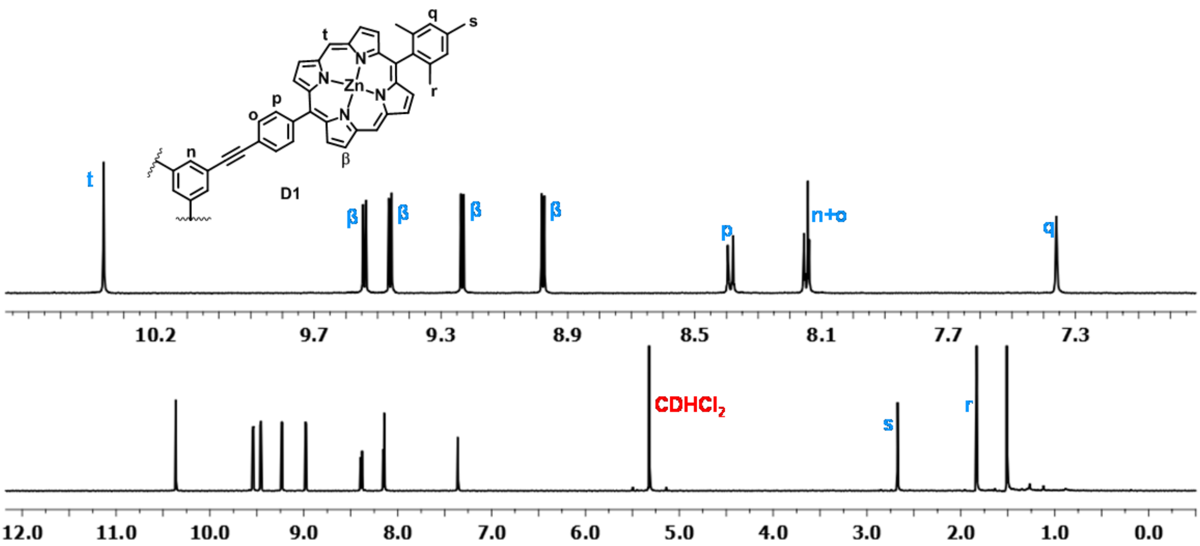


Figure S1. ^1H NMR of deck **D1** in CD_2Cl_2 (400 MHz, 298 K).

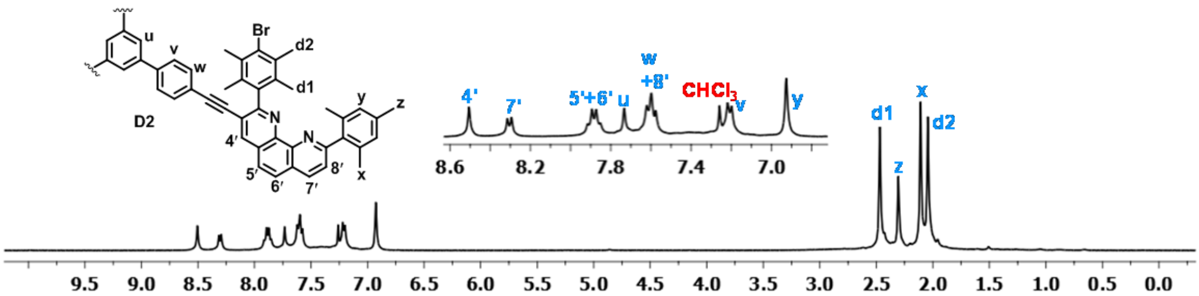


Figure S2. ^1H NMR of deck **D2** in $CDCl_3$ (400 MHz, 298 K).

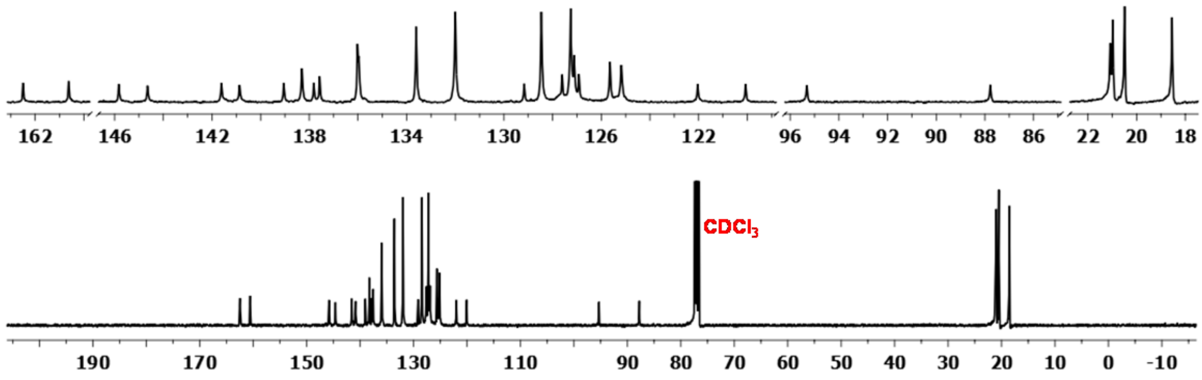


Figure S3. [13]C NMR of deck **D2** in $CDCl_3$ (100 MHz, 298 K).

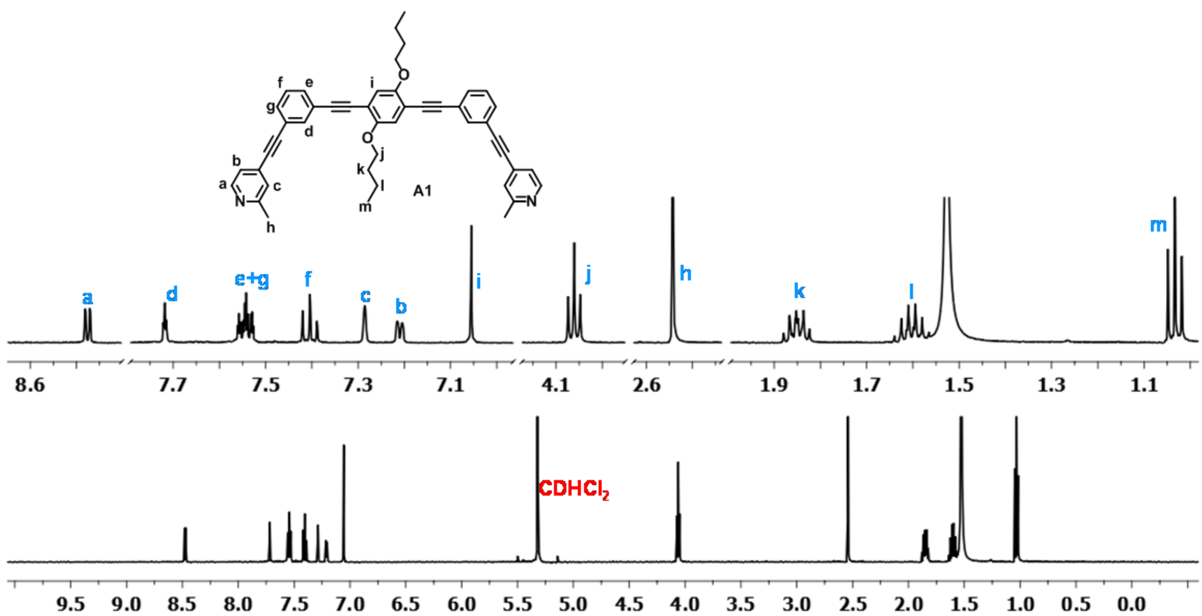


Figure S4. [1]H NMR of biped **A1** in CD_2Cl_2 (400 MHz, 298 K).

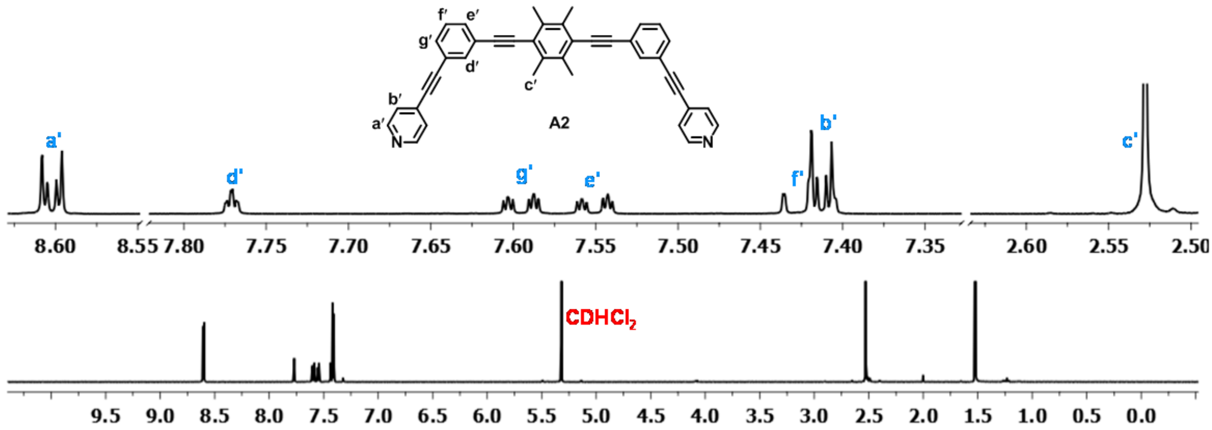


Figure S5. ^{1}H NMR of biped **A2** in CD_2Cl_2 (400 MHz, 298 K).

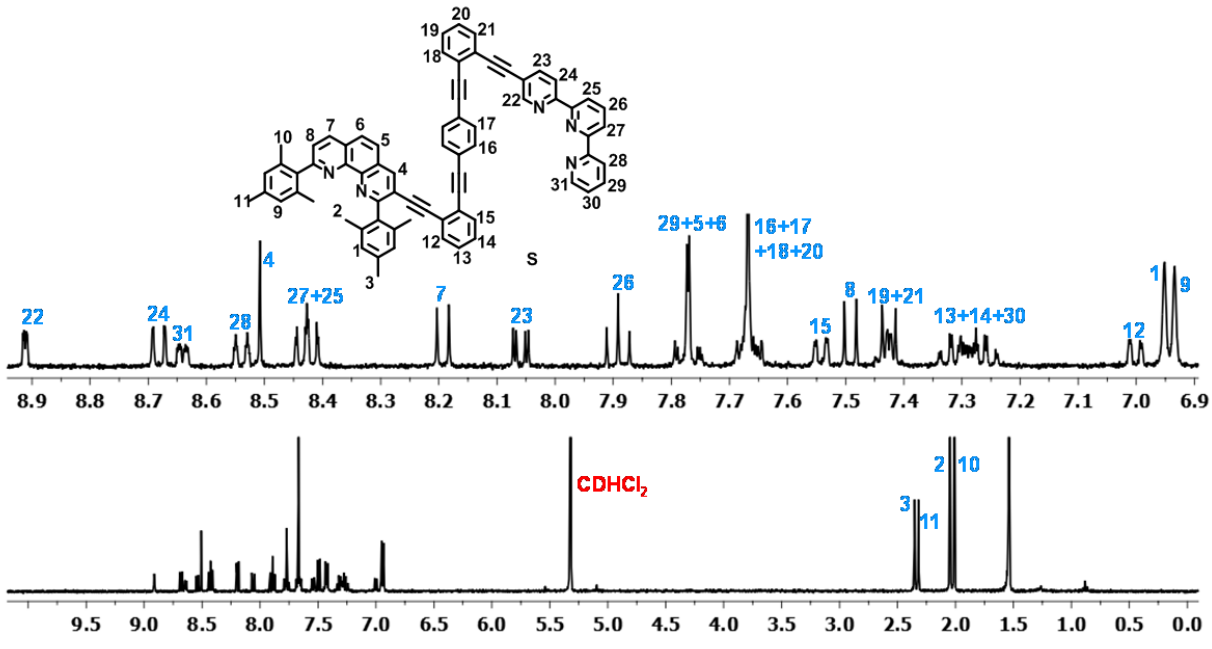


Figure S6. ^{1}H NMR of switch **S** in CD_2Cl_2 (400 MHz, 298 K).

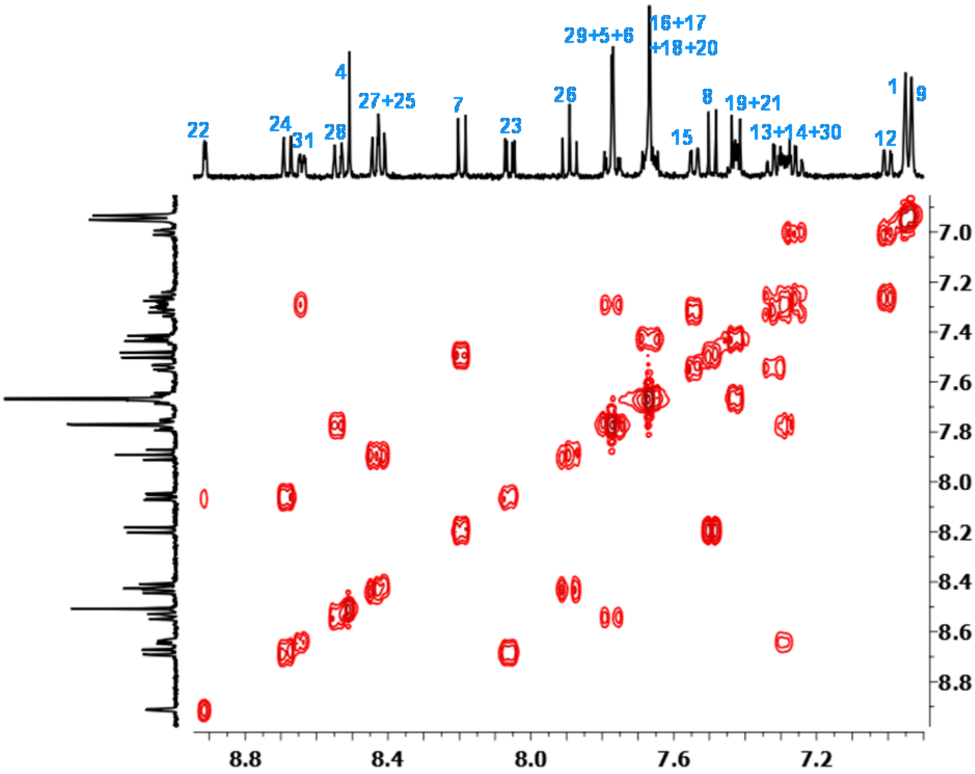


Figure S7. ^{1}H-^{1}H COSY NMR of switch **S** in CD_2Cl_2 (400 MHz, 298 K).

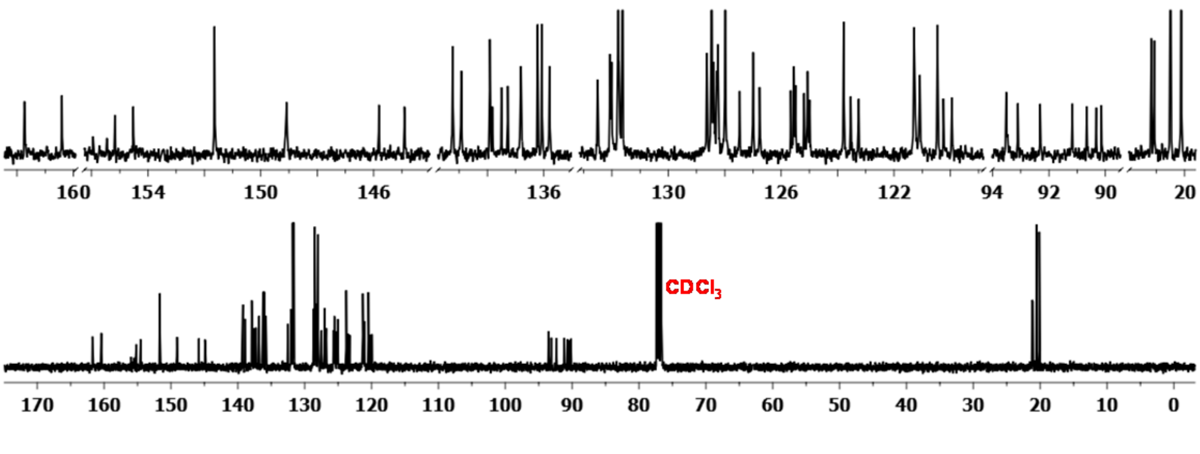


Figure S8. ^{13}C NMR of switch **S** in $CDCl_3$ (100 MHz, 298 K).

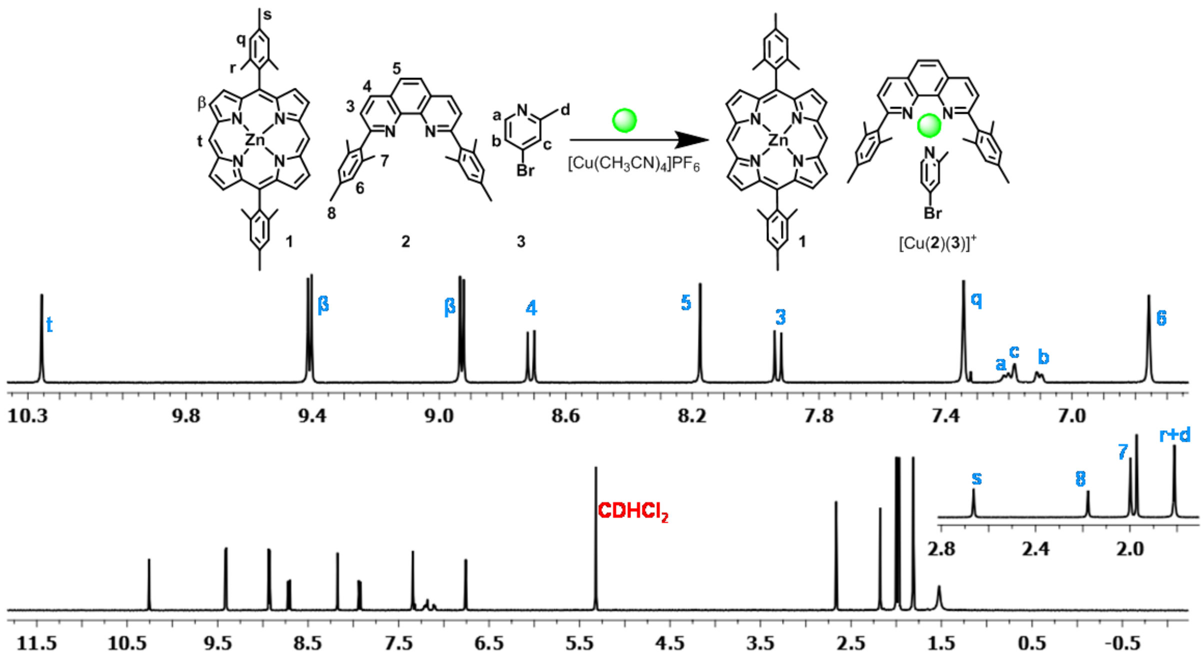


Figure S9. ^{1}H NMR of the 1:1:1:1 mixture of **1**, **2**, **3** and $[Cu(CH_3CN)_4]PF_6$ in CD_2Cl_2 (400 MHz, 298 K).

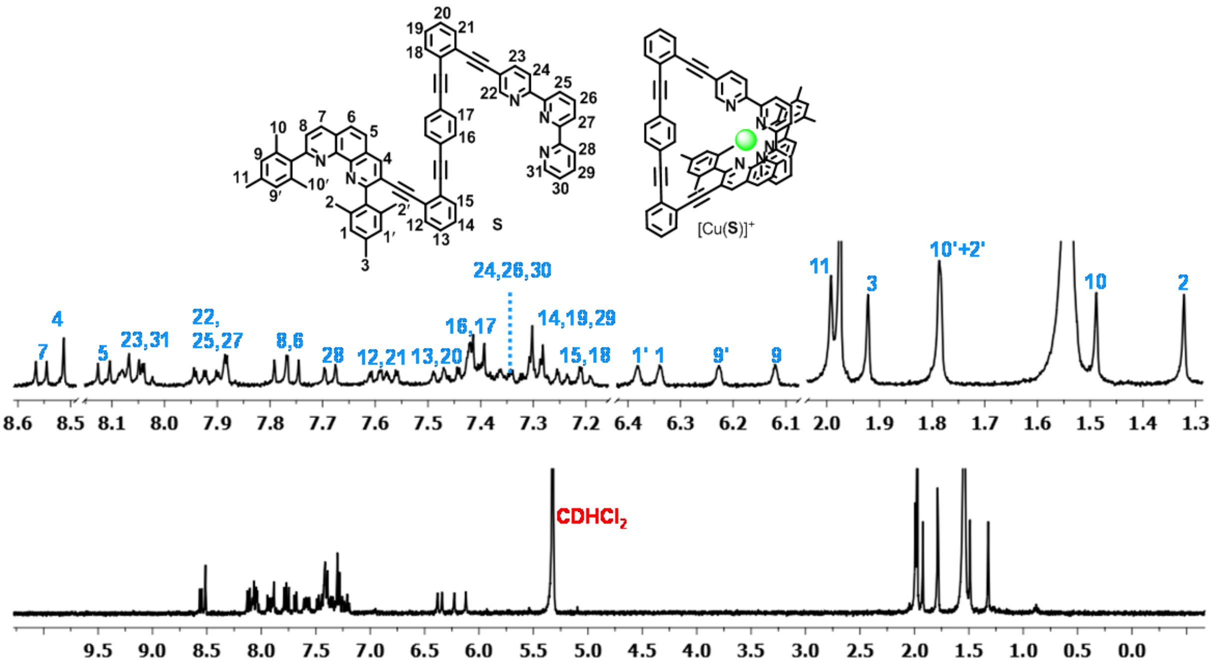


Figure S10. ^{1}H NMR of complex $[Cu(\mathbf{S})]^+$ in CD_2Cl_2 (400 MHz, 298 K).

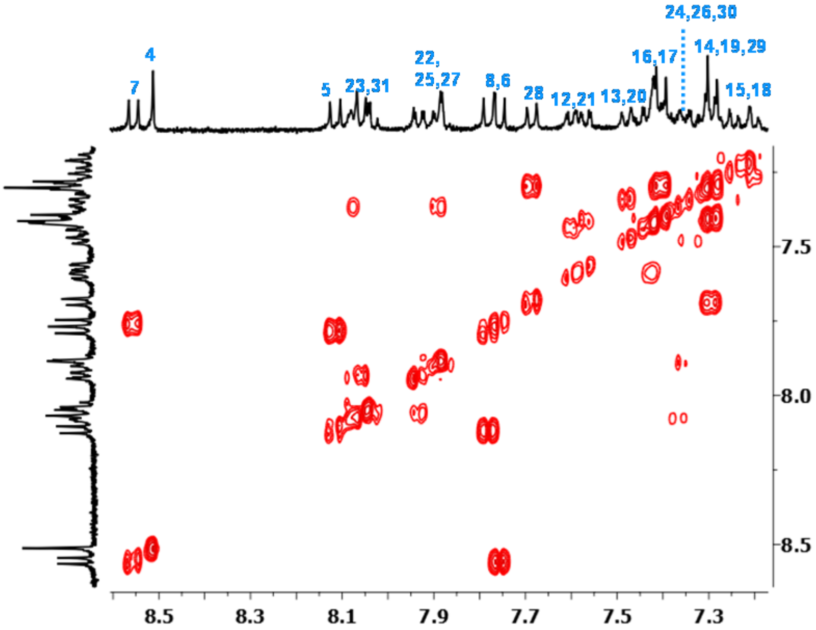


Figure S11. ^{1}H-^{1}H COSY NMR of complex $[Cu(\mathbf{S})]^{+}$ in CD_2Cl_2 (400 MHz, 298 K).

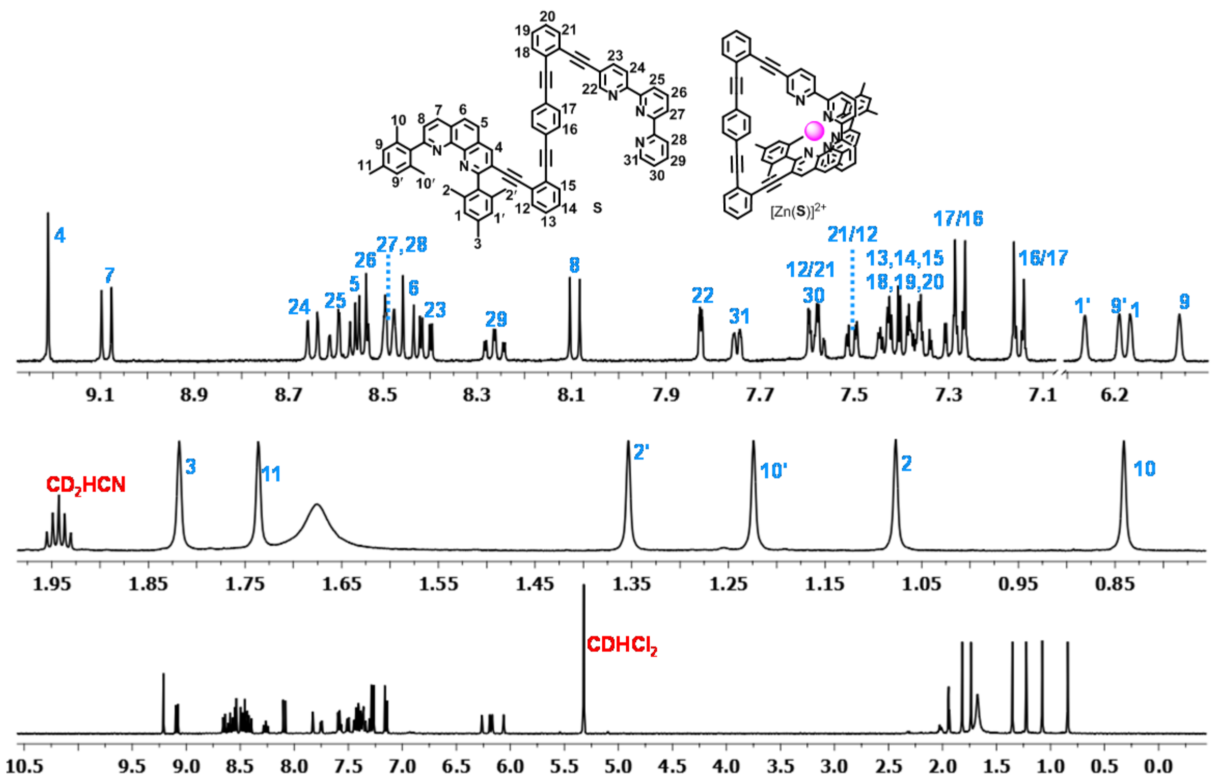


Figure S12. ^{1}H NMR of complex $[Zn(\mathbf{S})]^{2+}$ in CD_2Cl_2 (400 MHz, 298 K).

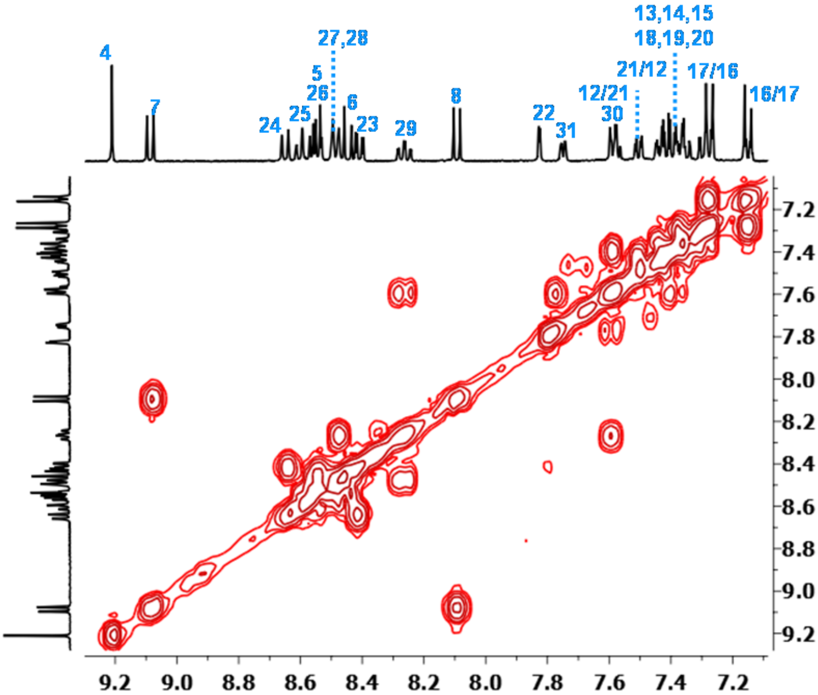


Figure S13. ^1H-^1H COSY NMR of complex $[Zn(\mathbf{S})]^{2+}$ in CD_2Cl_2 (400 MHz, 298 K).

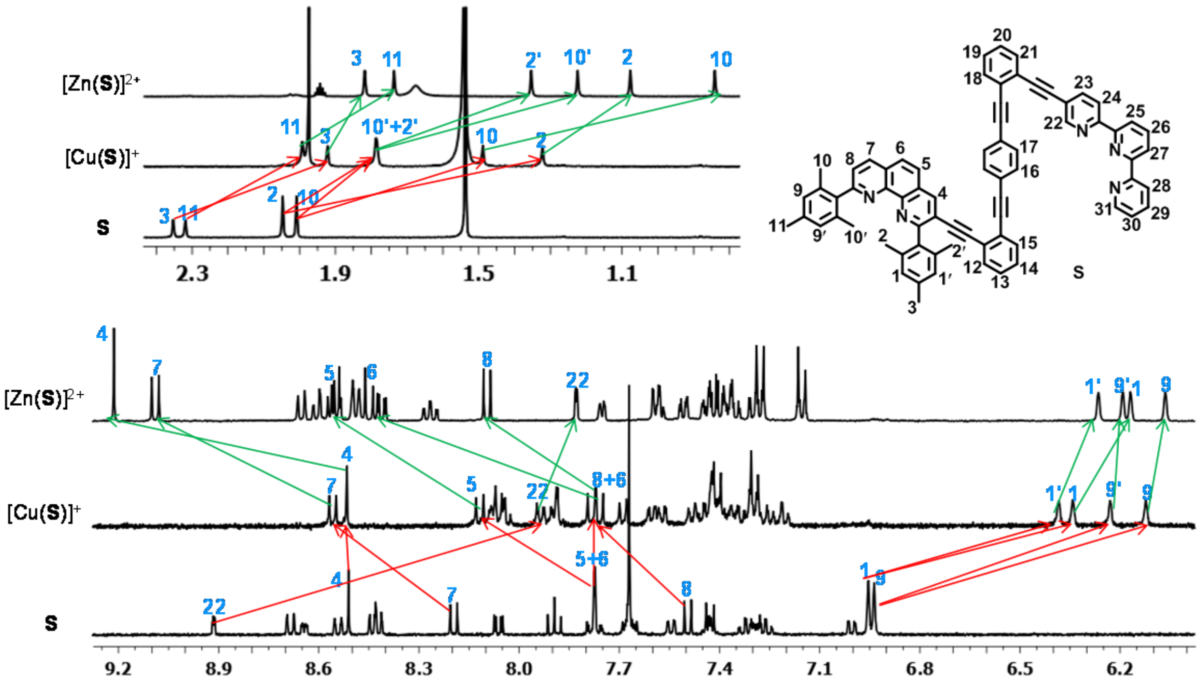


Figure S14. Comparison ^1H NMR of switch **S**, complex $[Cu(\mathbf{S})]^{+}$, $[Zn(\mathbf{S})]^{2+}$ in CD_2Cl_2 (400 MHz, 298 K).

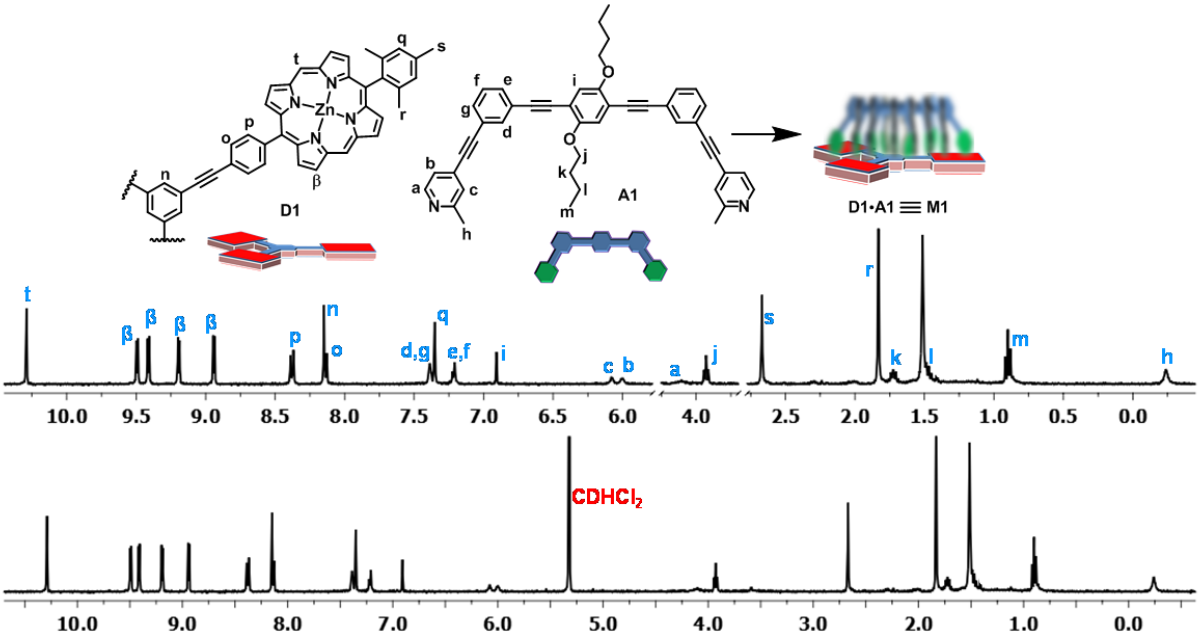


Figure S15. ^{1}H NMR of nanoslider **D1•A1** (**M1**) in CD_2Cl_2 (400 MHz, 298 K).

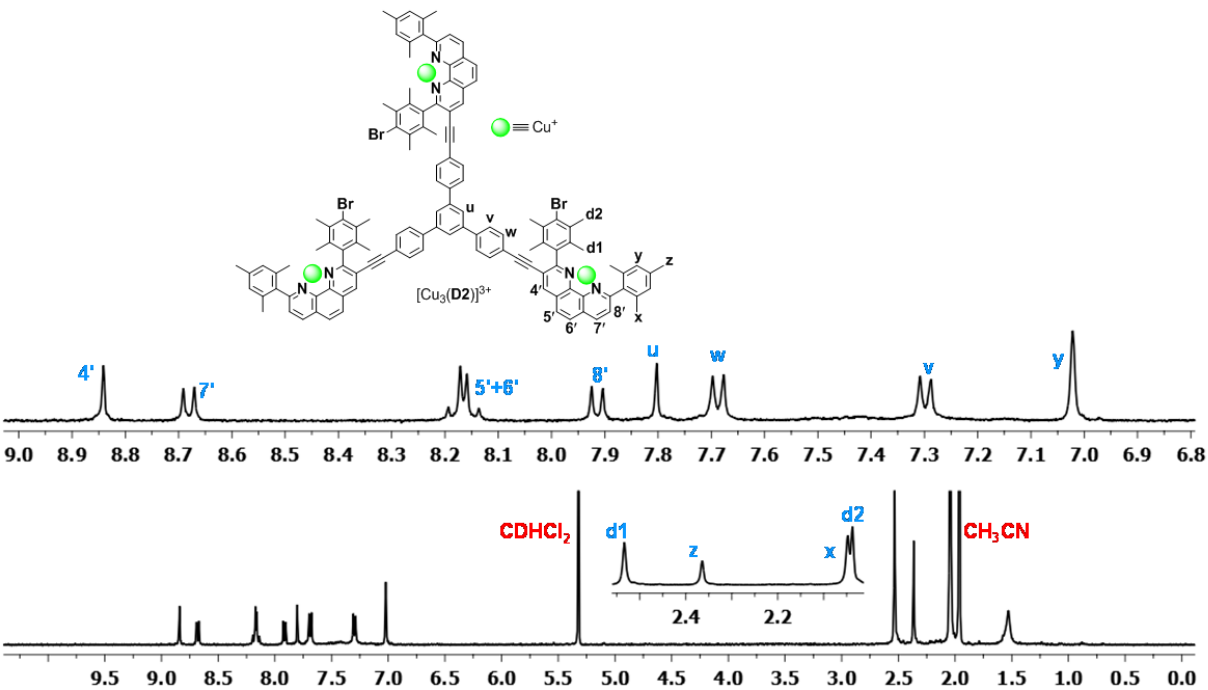


Figure S16. ^{1}H NMR of complex $[Cu_3(\mathbf{D2})]^{3+}$ in CD_2Cl_2 (400 MHz, 298 K).

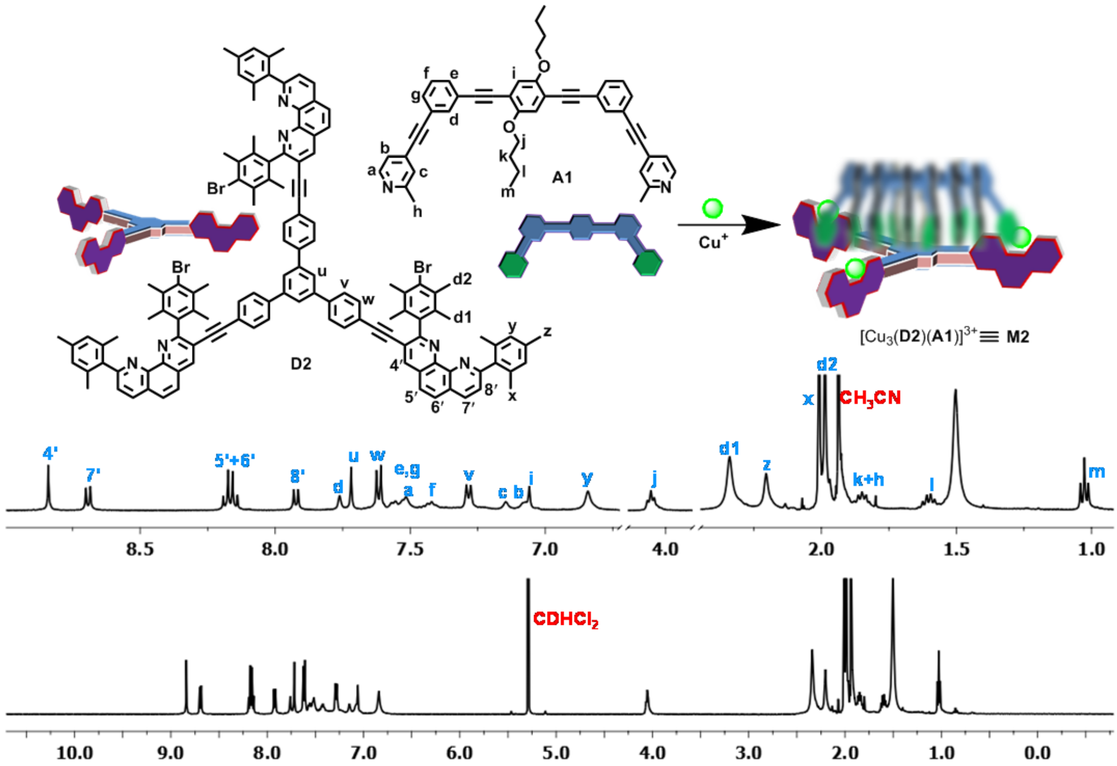


Figure S17. ^{1}H NMR of nanoslider $[Cu_3(\mathbf{D2})(\mathbf{A1})]^{3+}$ (= **M2**) in CD_2Cl_2 (400 MHz, 298 K).

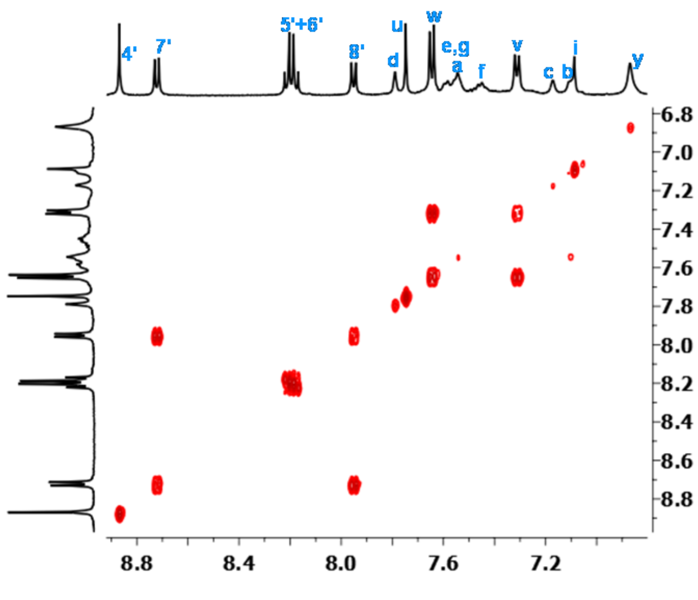


Figure S18. ^{1}H-^{1}H COSY NMR of nanoslider $[Cu_3(\mathbf{D2})(\mathbf{A1})]^{3+}$ (= **M2**) in CD_2Cl_2 (400 MHz, 298 K).

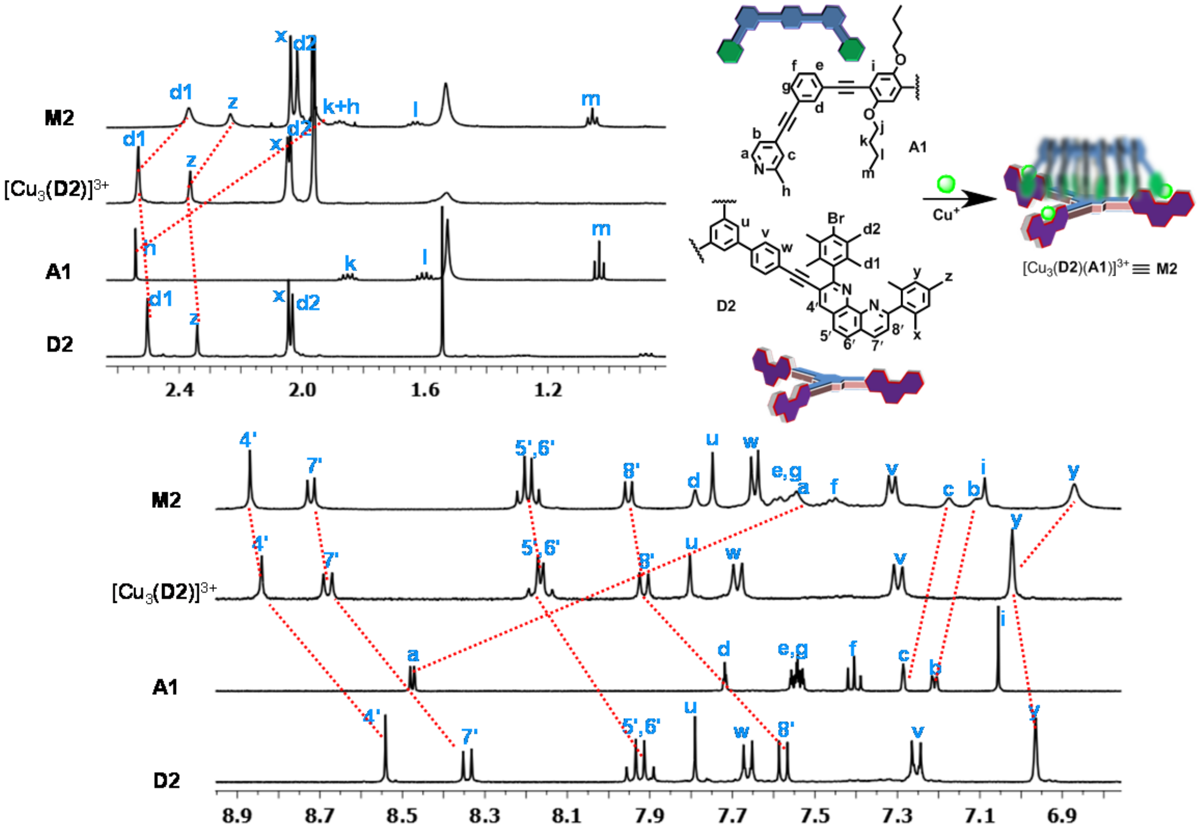


Figure S19. Comparison ^{1}H NMR of deck **D2**, biped **A1**, complex $[Cu_3(\mathbf{D2})]^{3+}$, nanoslider $[Cu_3(\mathbf{D2})(\mathbf{A1})]^{3+}$ (= **M2**) in CD_2Cl_2 (400 MHz, 298 K).

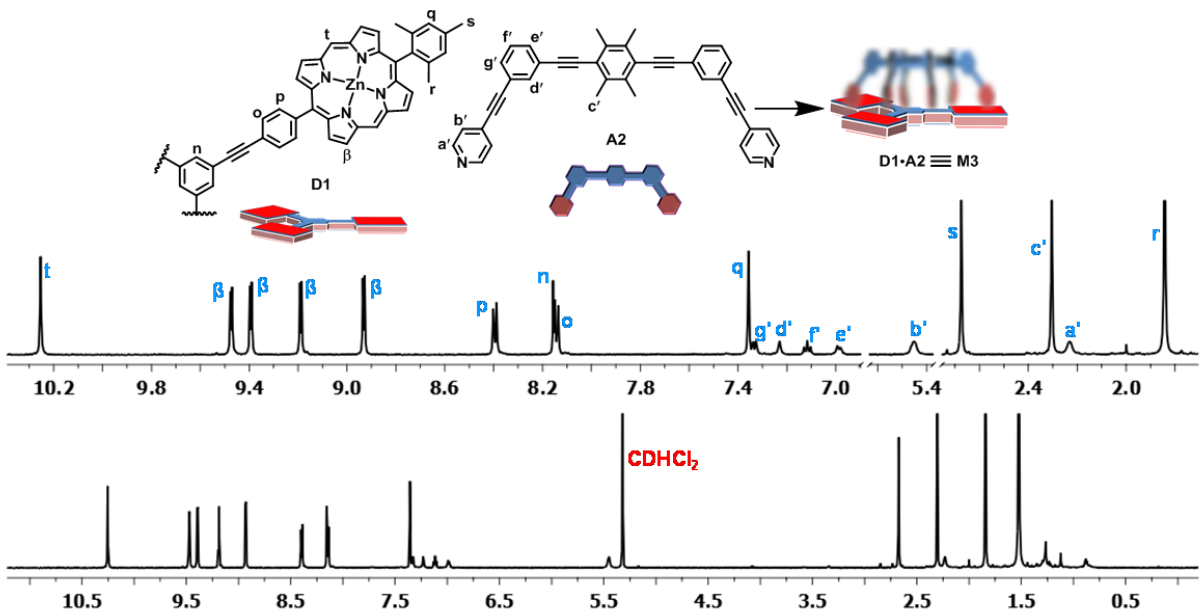


Figure S20. ^{1}H NMR of nanoslider **D1•A2** (= **M3**) in CD_2Cl_2 (400 MHz, 298 K).

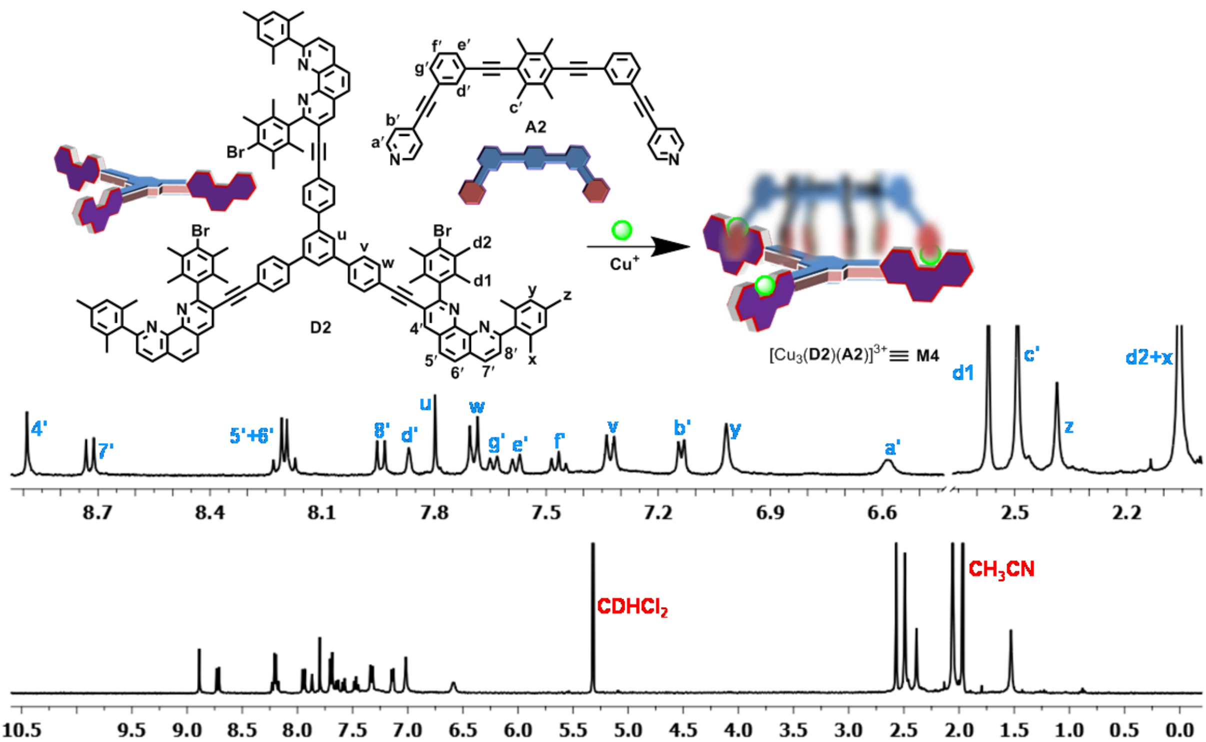


Figure S21. ^{1}H NMR of nanoslider $[Cu_3($**D2**$)($**A2**$)]^{3+}$ (= **M4**) in CD_2Cl_2 (400 MHz, 298 K).

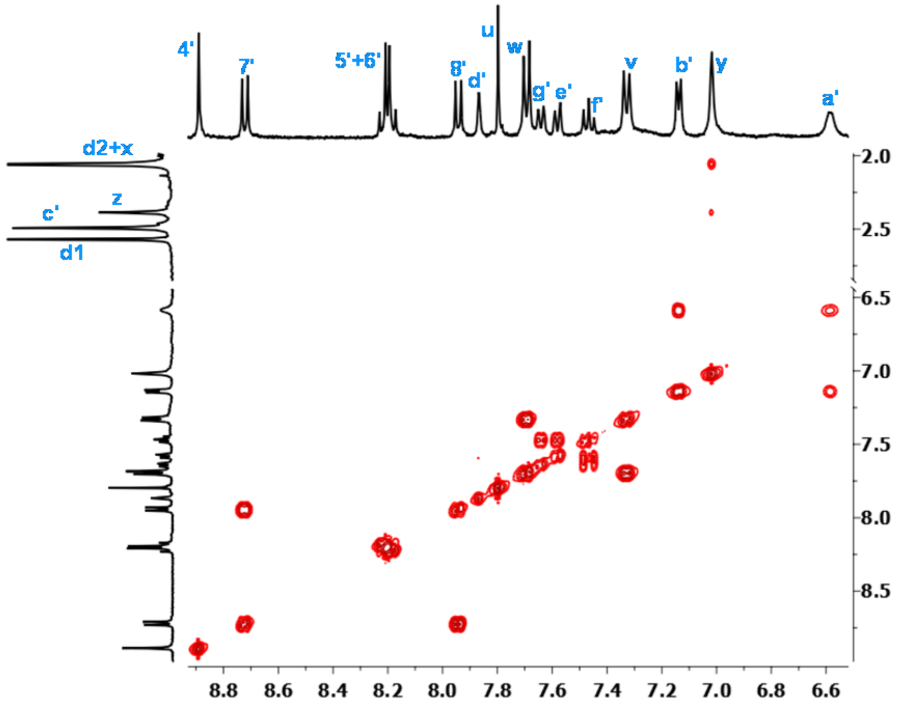


Figure S22. ^{1}H-^{1}H COSY NMR of nanoslider $[Cu_3(\mathbf{D2})(\mathbf{A2})]^{3+}$ (= **M4**) in CD_2Cl_2 (400 MHz, 298 K).

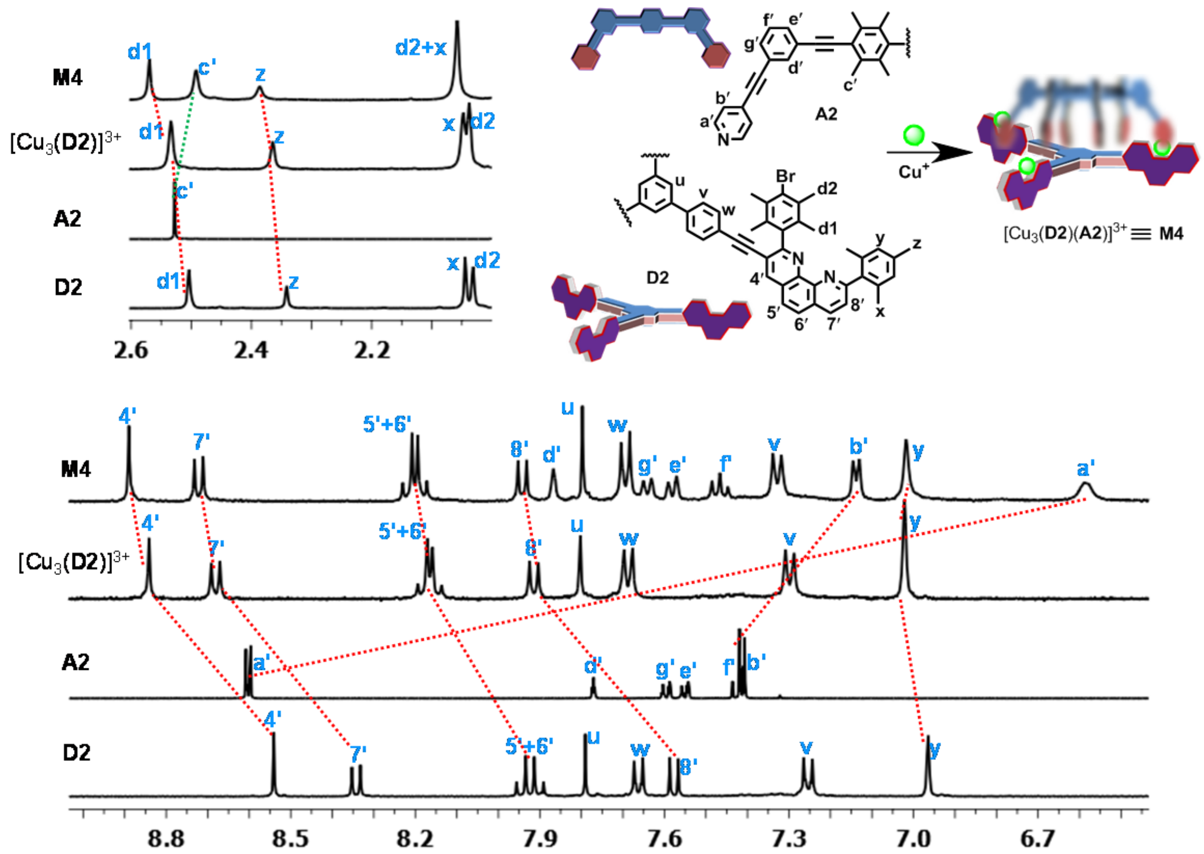


Figure S23. Comparison ^{1}H NMR of deck **D2**, biped **A2**, complex $[Cu_3(\mathbf{D2})]^{3+}$, nanoslider $[Cu_3(\mathbf{D2})(\mathbf{A2})]^{3+}$ (= **M4**) in CD_2Cl_2 (400 MHz, 298 K).

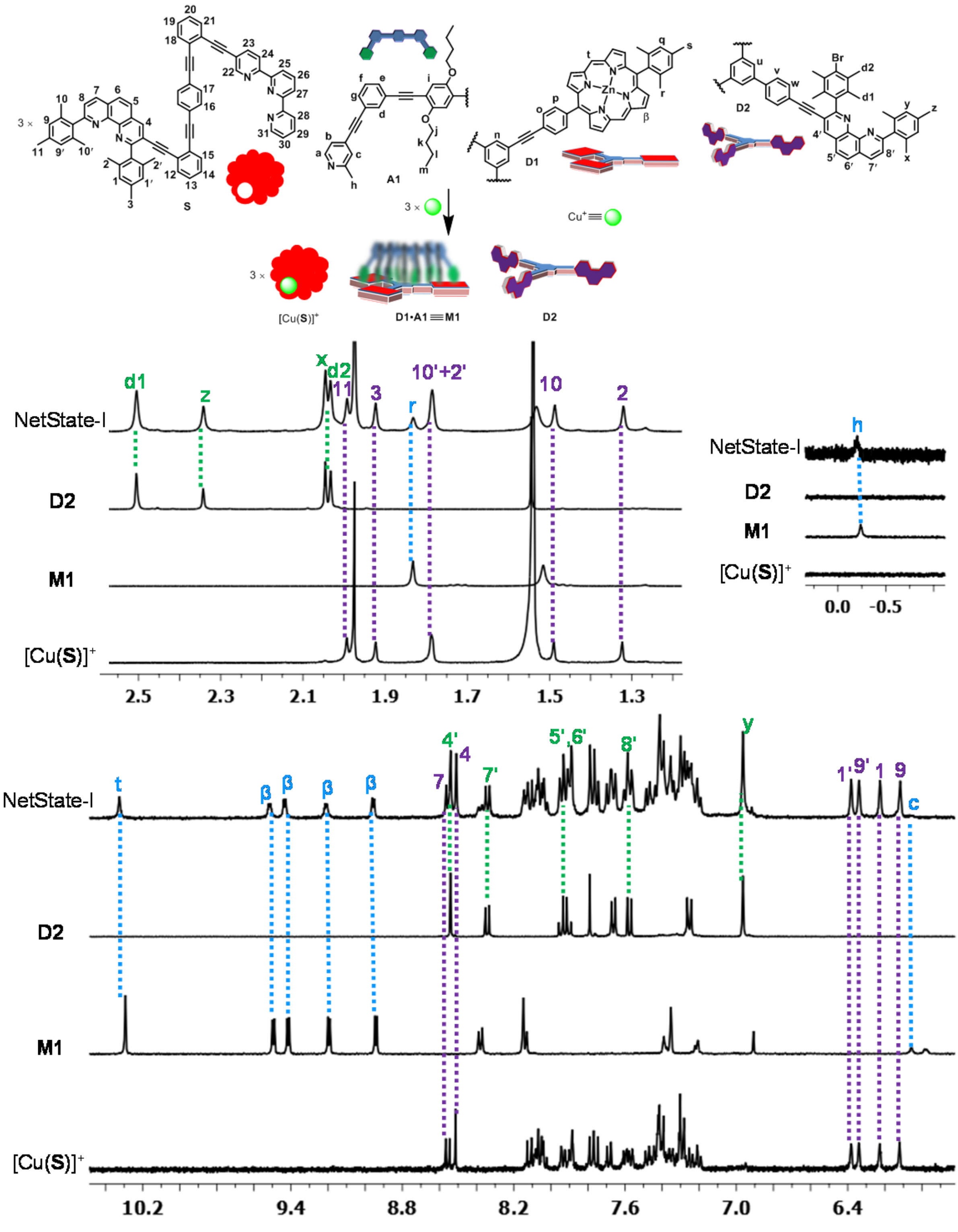


Figure S24. Comparison [1]H NMR of complex $[Cu(\mathbf{S})]^+$, nanoslider **D1•A1** (= **M1**), deck **D2** and NetState-I in CD_2Cl_2 (400 MHz, 298 K).

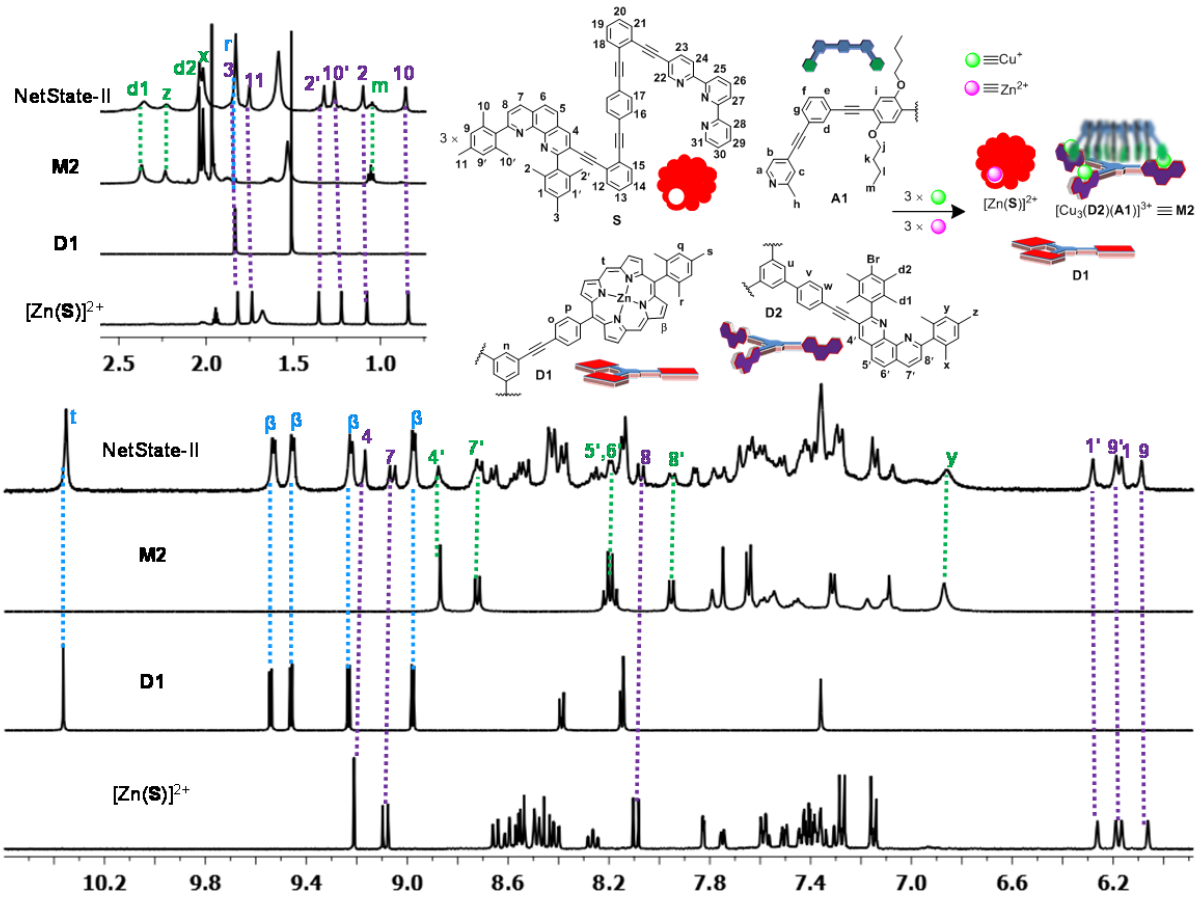


Figure S25. Comparison [1]H NMR of complex $[Zn(\mathbf{S})]^{2+}$, deck **D1**, nanoslider $[Cu_3(\mathbf{D2})(\mathbf{A1})]^{3+}$ (= **M2**) and NetState-II in CD_2Cl_2 (400 MHz, 298 K).

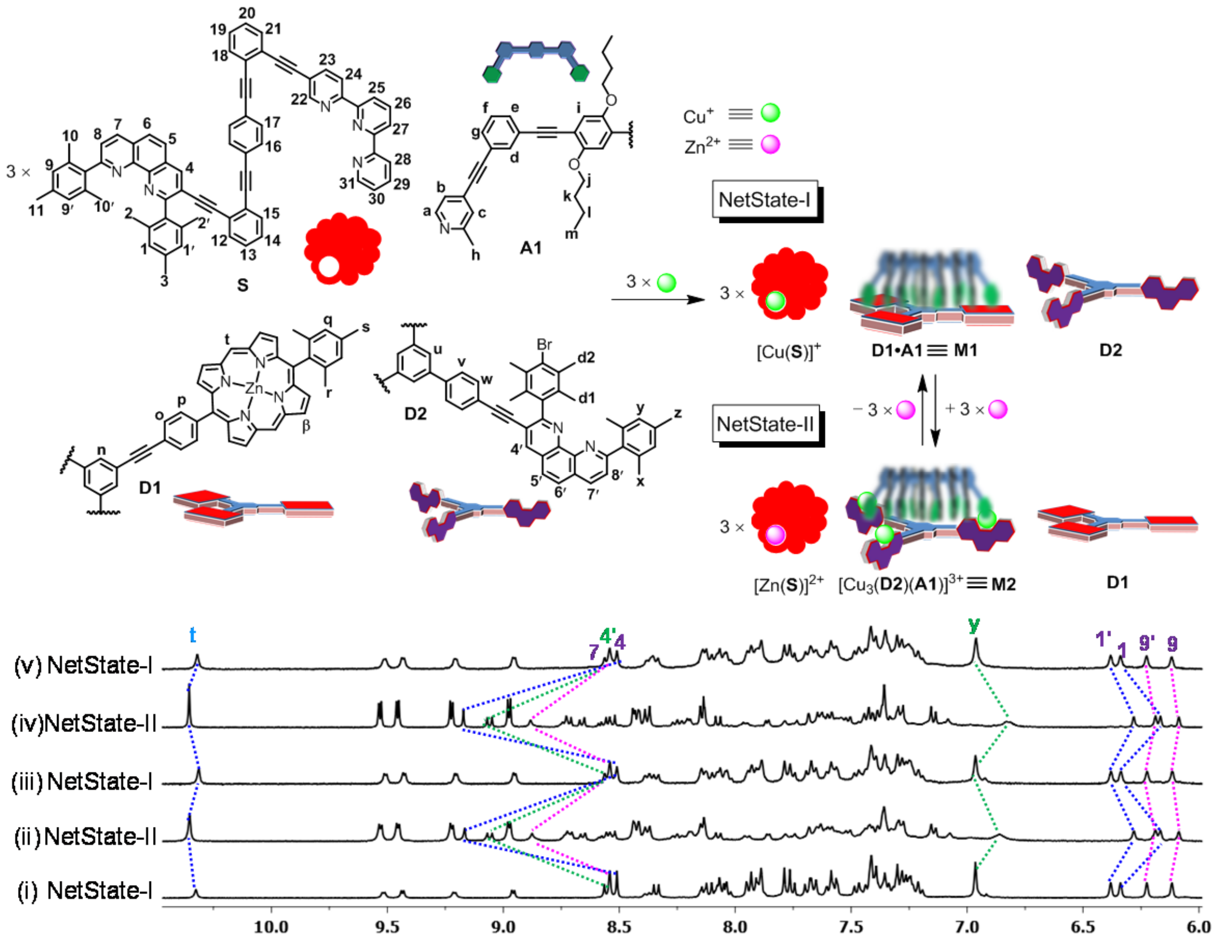


Figure S26. Partial ^{1}H NMR (400 MHz, 298 K) shows the reversible interconversion of NetState-I and NetState-II over two complete cycles in CD_2Cl_2. (i) NetState-I was obtained by mixing of **S**, **D1**, **D2**, **A1** and Cu^+ (3:1:1:1:3) in CD_2Cl_2. (ii) Addition of 3.0 equiv. of Zn^{2+} to NetState-I furnished NetState-II. (iii) Addition of 3.0 equiv. of hexacyclen to NetState-II. (iv) Addition of 3.0 equiv. of Zn^{2+} to (iii) regenerated NetState-II. (v) NetState-I was regenerated from (iv) by addition of 3.0 equiv. of hexacyclen.

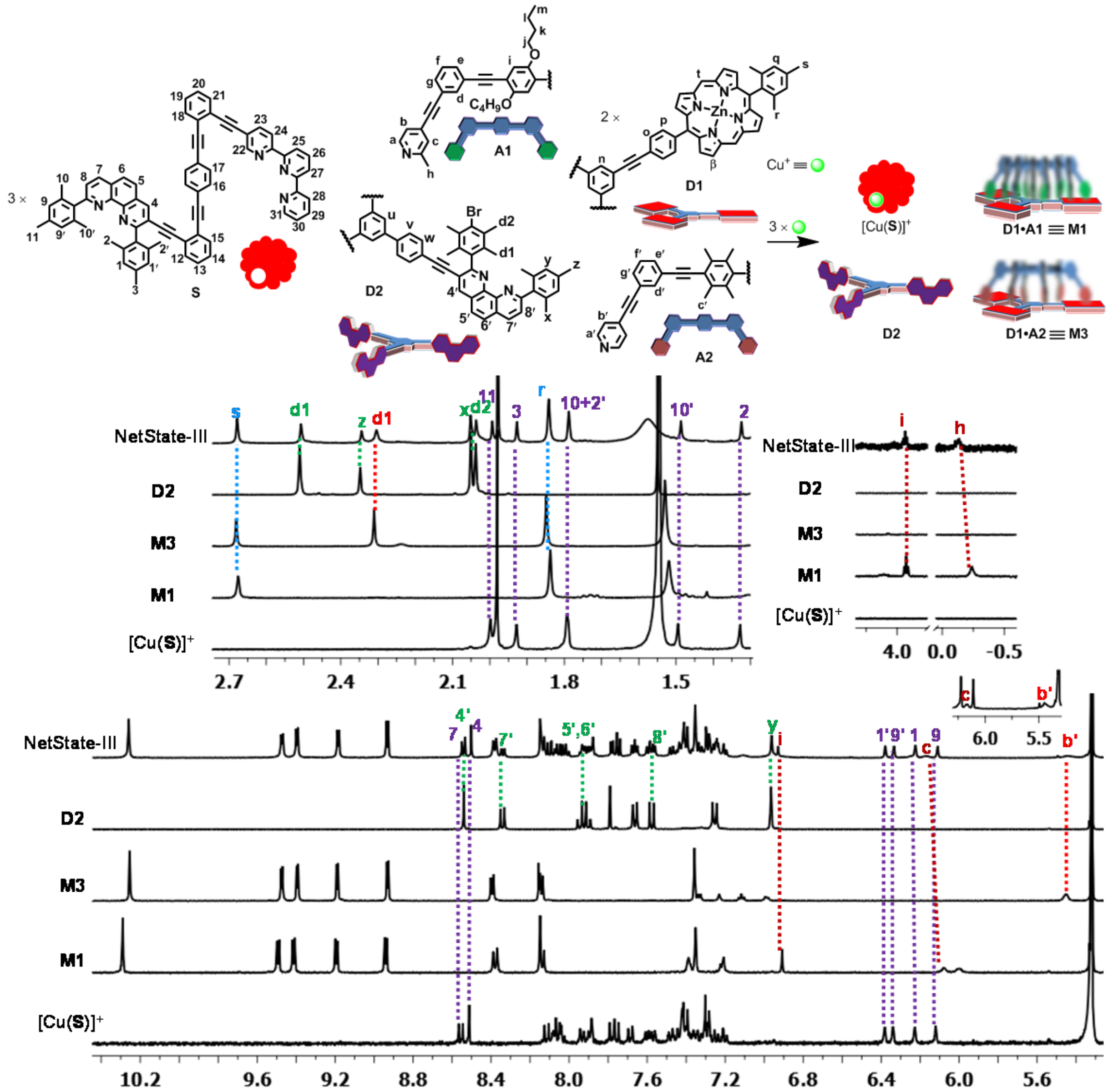


Figure S27. Comparison of ^{1}H NMR spectra (400 MHz, 298 K, CD_2Cl_2) of complex $[Cu(\mathbf{S})]^+$, nanoslider **D1•A1** (= **M1**), **D1•A2** (= **M3**), deck **D2** and NetState-III.

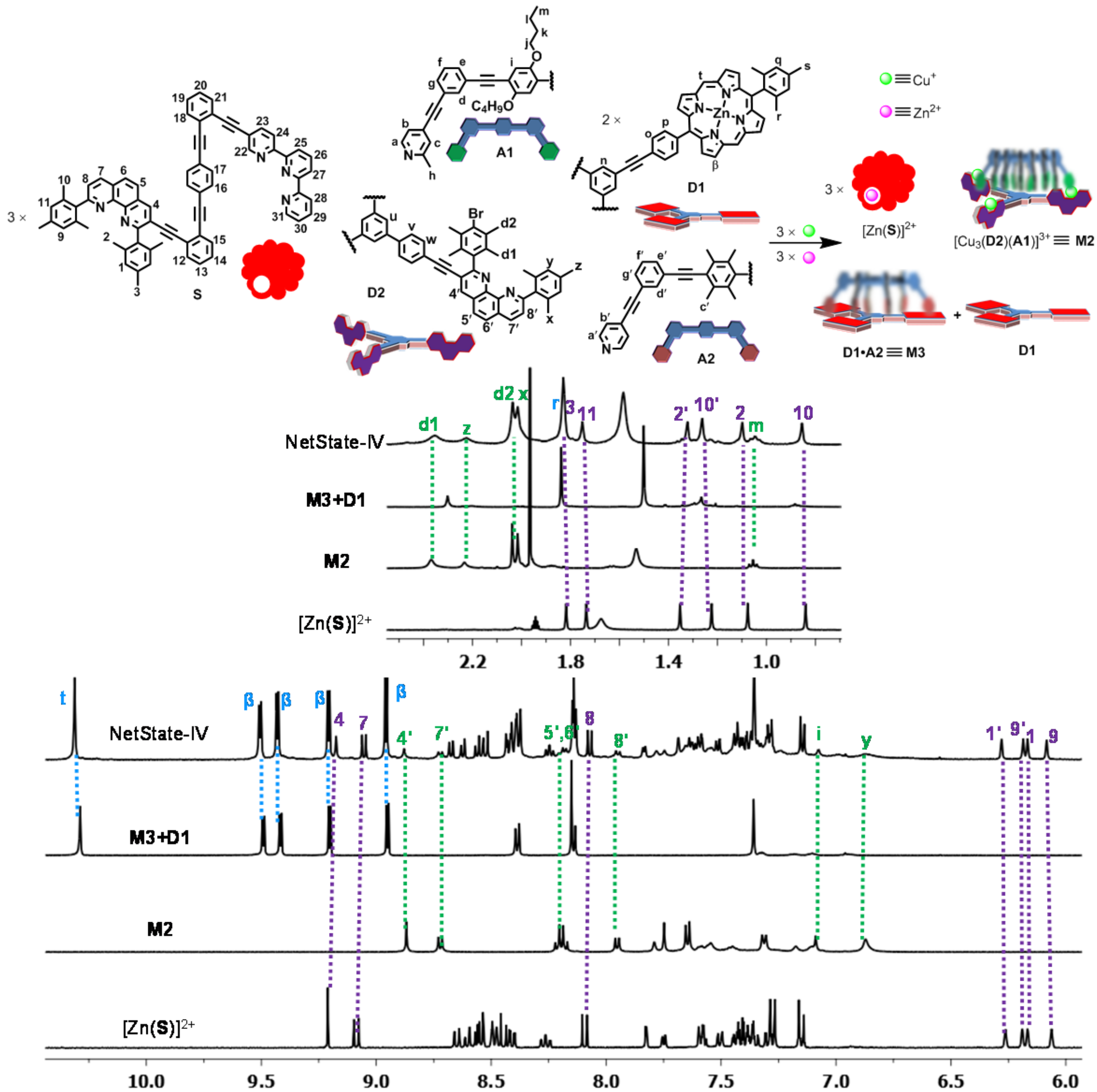


Figure S28. Comparison ^{1}H NMR of complex $[Zn(\mathbf{S})]^{2+}$, nanoslider $[Cu_3(\mathbf{D2})(\mathbf{A1})]^{3+}$ (= **M2**), **D1•A2** (= **M3**) + **D1** and NetState-IV in CD_2Cl_2 (400 MHz, 298 K).

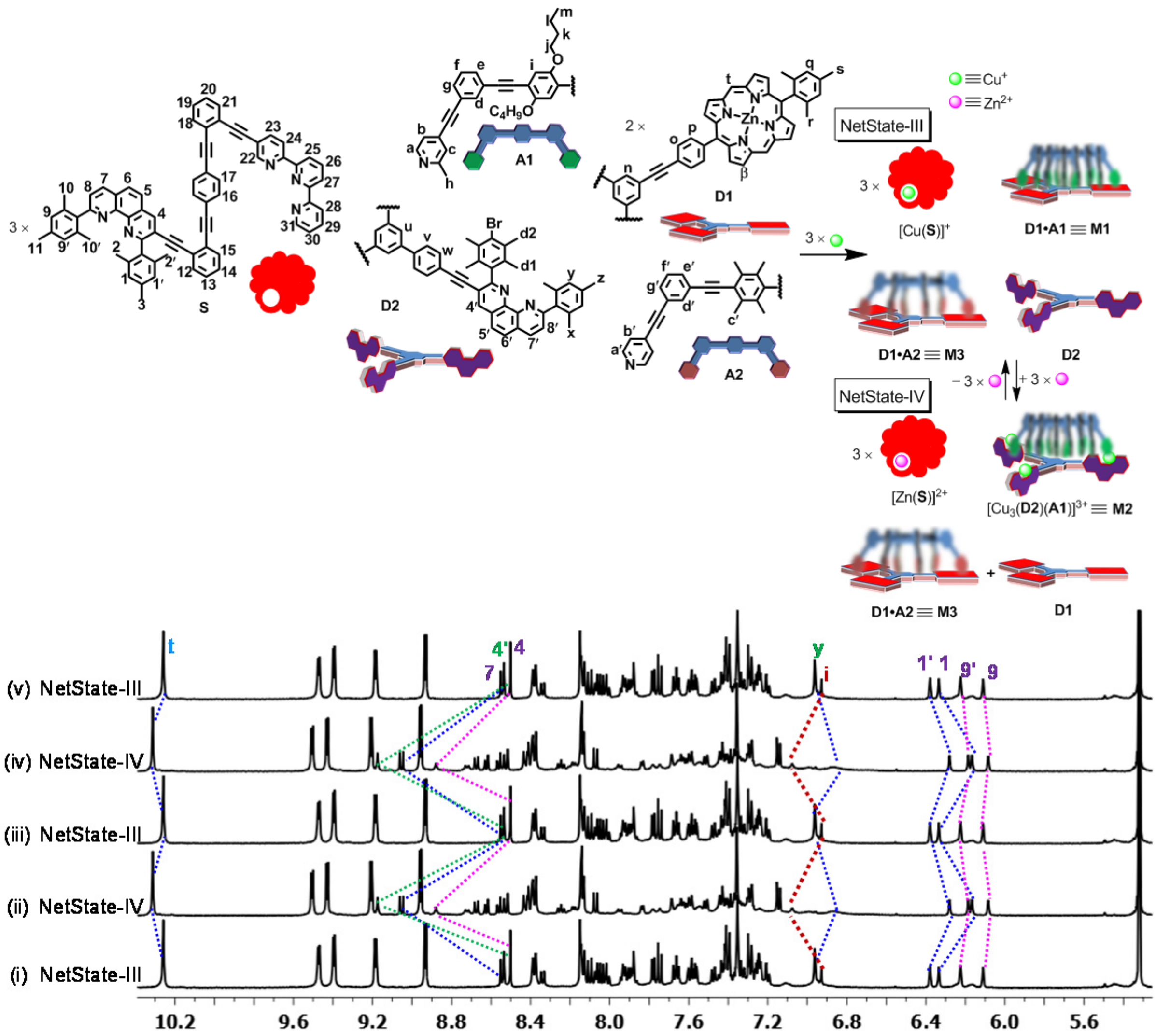


Figure S29. Partial ^{1}H NMR (400 MHz, 298 K) shows the reversible interconversion of NetState-III and NetState-IV over two complete cycles in CD_2Cl_2. (i) NetState-III was obtained by mixing of **S**, **D1**, **D2**, **A1**, **A2** and Cu^{+} (3:2:1:1:1:3) in CD_2Cl_2. (ii) Addition of 3.0 equiv. of Zn^{2+} to NetState-III furnished NetState-IV. (iii) Addition of 3.0 equiv. of hexacyclen to NetState-IV. (iv) Addition of 3.0 equiv. of Zn^{2+} to (iii) regenerated NetState-IV. (v) NetState-III was regenerated from (iv) by addition of 3.0 equiv. of hexacyclen.

3. Variable Temperature ^{1}H NMR Spectra

The rate constants of sliding at various temperatures were determined using the program WinDNMR through simulation of the experimental ^{1}H NMR spectra. The spectra simulation was performed using the model of a 2-spin system undergoing mutual exchange. Activation parameters were determined from an Eyring plot.

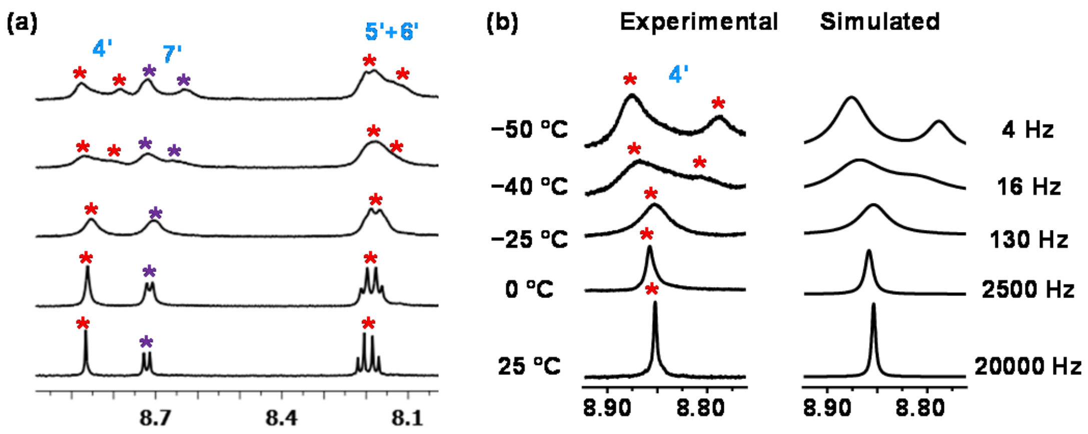


Figure S30. (a) VT ^{1}H NMR (600 MHz) of nanoslider $[Cu_3(\mathbf{D2})(\mathbf{A1})]^{3+}$ (= **M2**) in CD_2Cl_2 shows the splitting of protons (5'+6')-, 7'- and 4'-H in 2:1 ratio at different temperatures. (b) Experimental and simulated splitting of 4'-H at different temperatures. The corresponding rate constant was determined from the simulation.

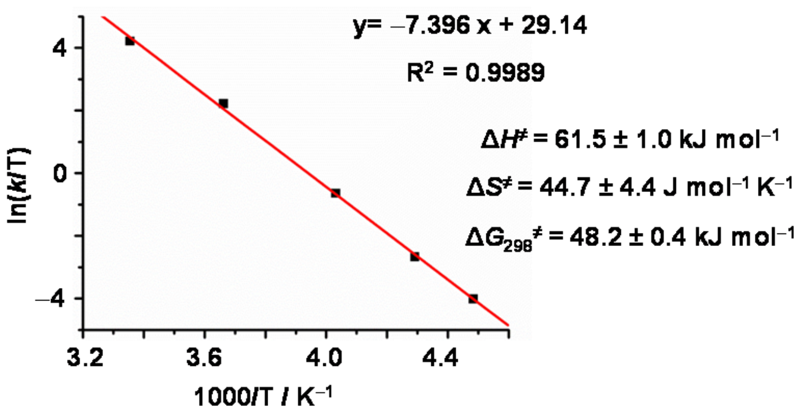


Figure S31. Eyring plot of the exchange motion in nanoslider $[Cu_3(\mathbf{D2})(\mathbf{A1})]^{3+}$ (= **M2**).

4. DOSY NMR Spectra

Calculation of hydrodynamic radius from:

DOSY: The diffusion coefficient D of nanoslider $[Cu_3(\mathbf{D2})(\mathbf{A1})]^{3+}$ (= **M2**) was obtained from the DOSY spectrum and the corresponding hydrodynamic radius was calculated by using the Stokes-Einstein equation:

$r = k_BT/6\pi\eta D$

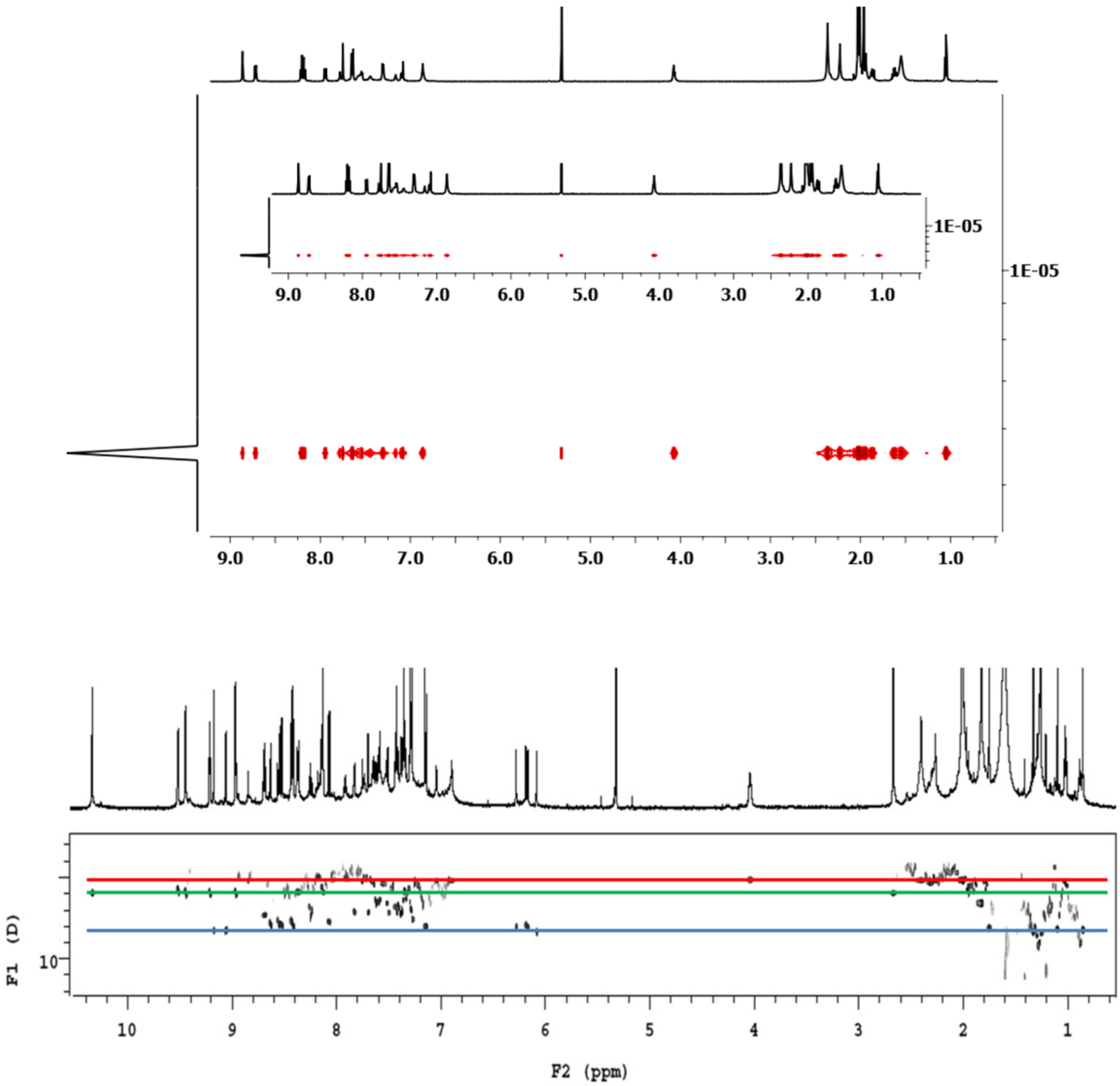


Figure S32. (top) DOSY NMR of nanoslider $[Cu_3(\mathbf{D2})(\mathbf{A1})]^{3+}$ (= **M2**) in CD_2Cl_2 (600 MHz, 298 K). Diffusion coefficient $D = 4.2 \times 10^{-10}$ m^2 s^{-1}, hydrodynamic radius r = 13 Å. (bottom) DOSY NMR of NetState-II in CD_2Cl_2 (600 MHz, 298 K) showing three different assemblies with close hydrodynamic radii.

5. ESI-MS Spectra

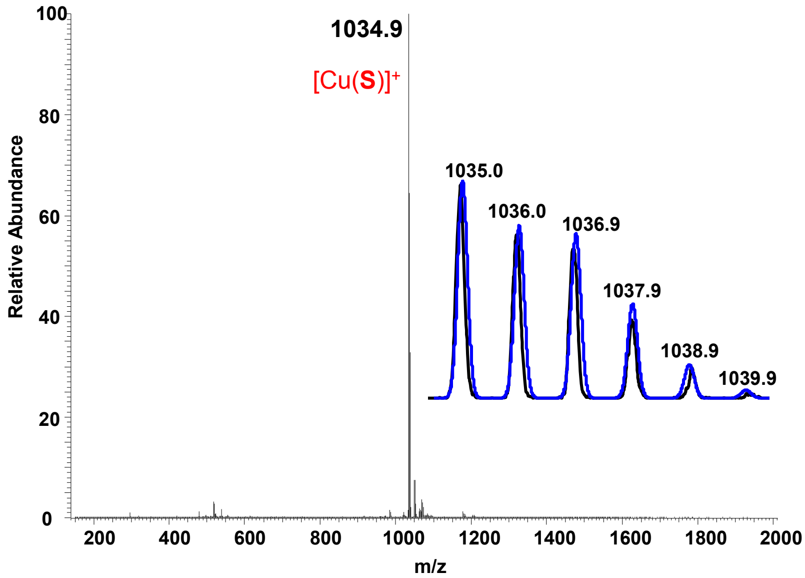


Figure S33. ESI-MS of complex [Cu(**S**)]$^{+}$.

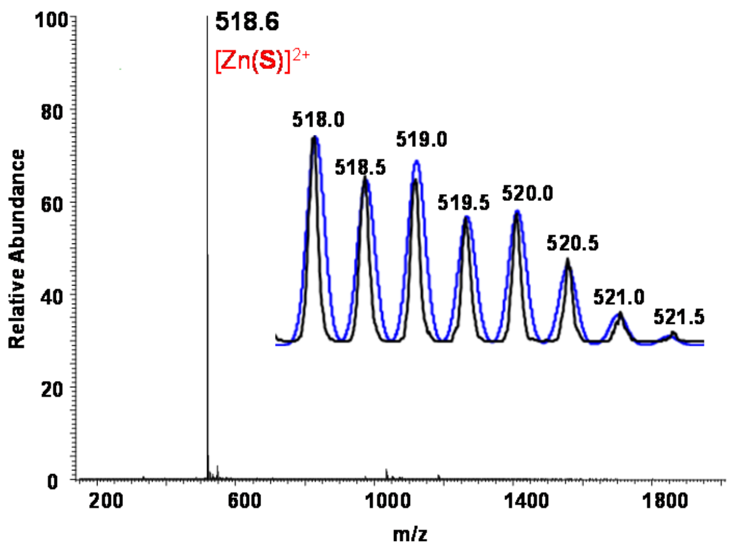


Figure S34. ESI-MS of complex [Zn(**S**)]$^{2+}$.

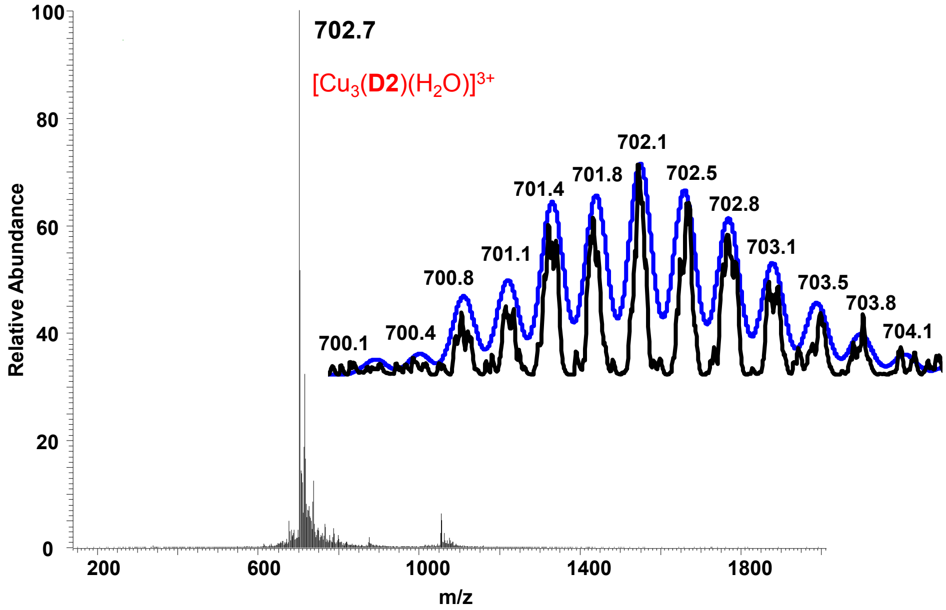


Figure S35. ESI-MS of complex $[Cu_3(\mathbf{D2})(H_2O)]^{3+}$.

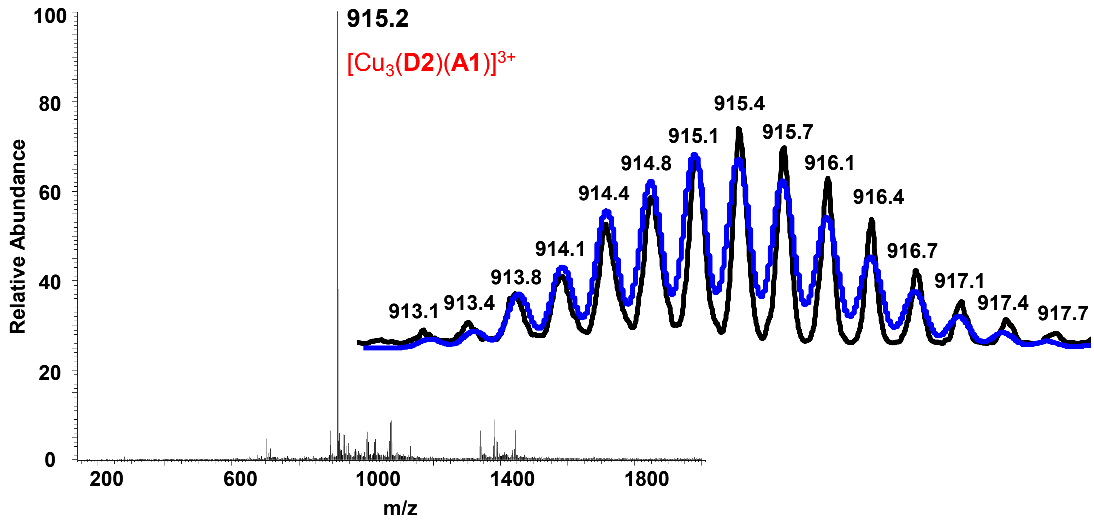


Figure S36. ESI-MS of nanoslider $[Cu_3(\mathbf{D2})(\mathbf{A1})]^{3+}$ (= **M2**).

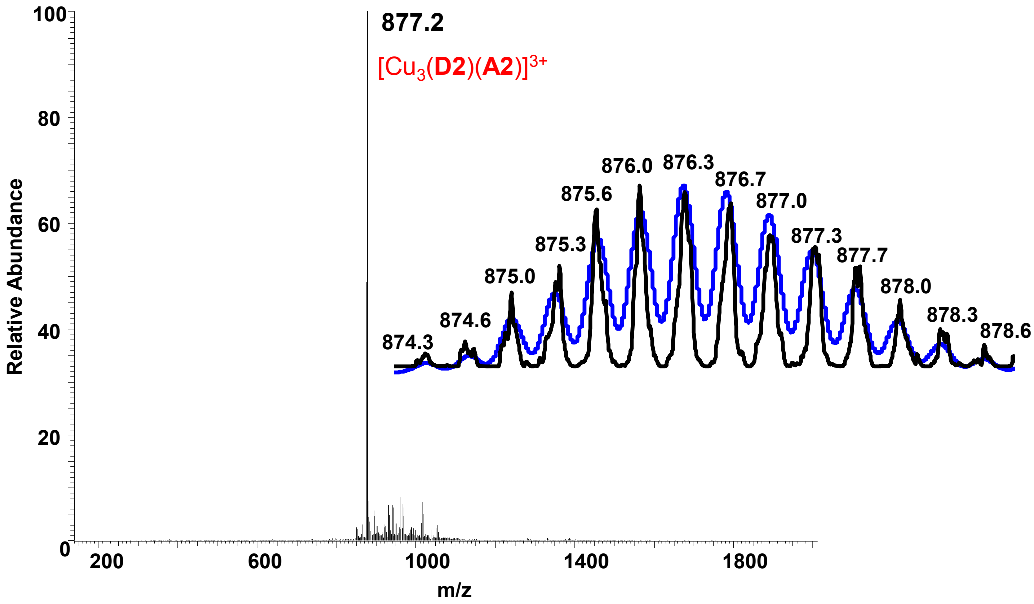


Figure S37. ESI-MS of nanoslider $[Cu_3(\mathbf{D2})(\mathbf{A2})]^{3+}$ (= **M4**).

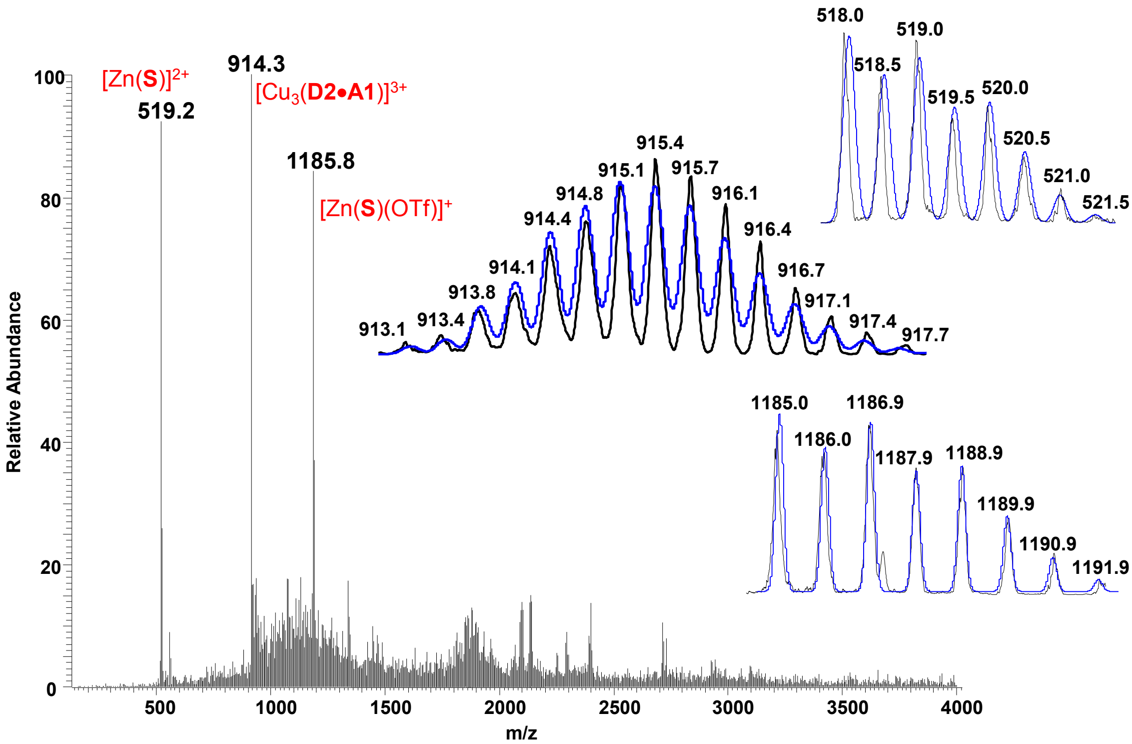


Figure S38. ESI-MS of NetState-II.

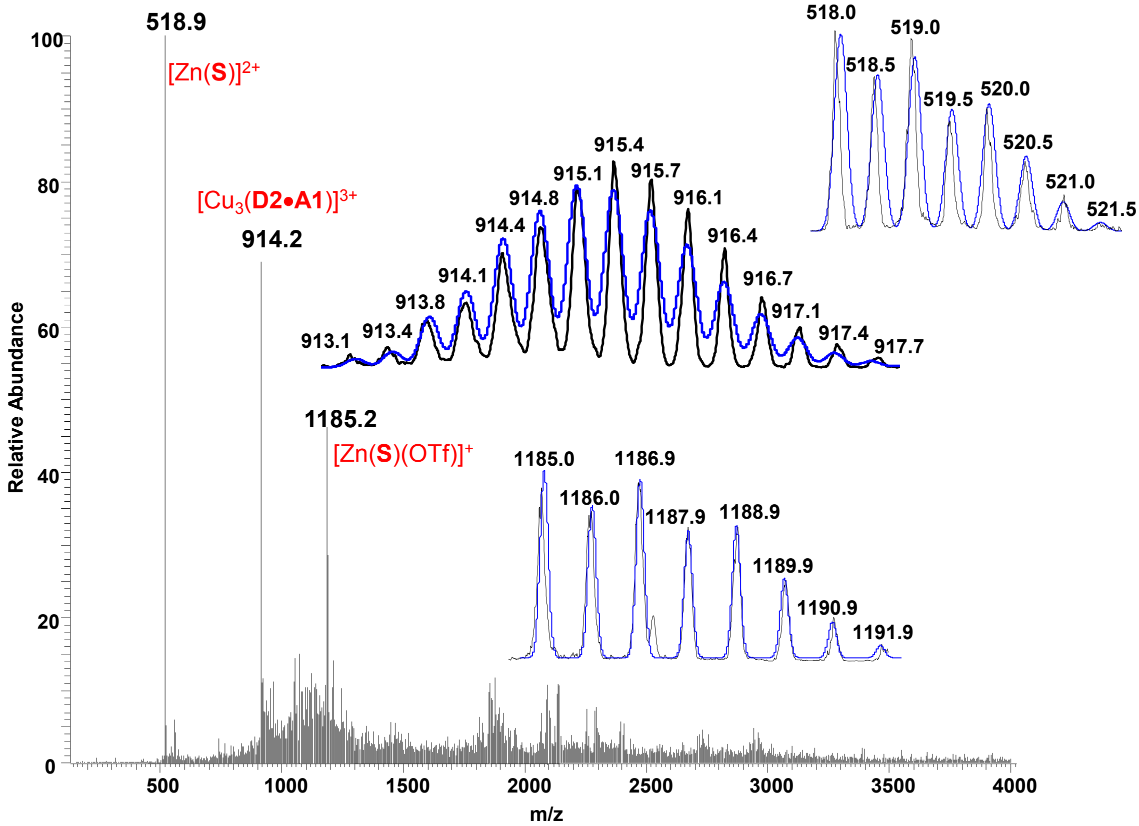


Figure S39. ESI-MS of NetState-IV.

6. UV-Vis Spectra

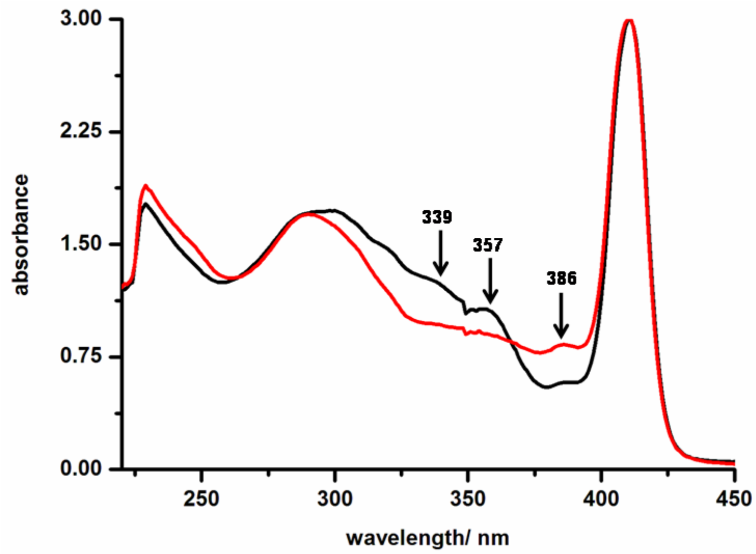


Figure S40. UV-Vis spectra of NetState-I (black line) and NetState-II (red line) in CH_2Cl_2 at 298 K ($c = 10^{-6}$ M).

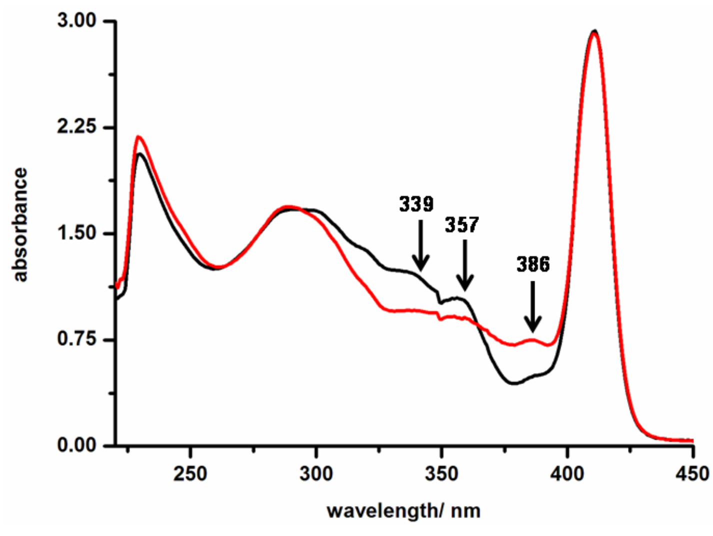


Figure S41. UV-Vis spectra of NetState-I (black line) and NetState-II (red line) in presence of 3.0 equiv of tetrabutylammonium iodide in CH_2Cl_2 at 298 K ($c = 10^{-6}$ M).

7. Kinetic Studies

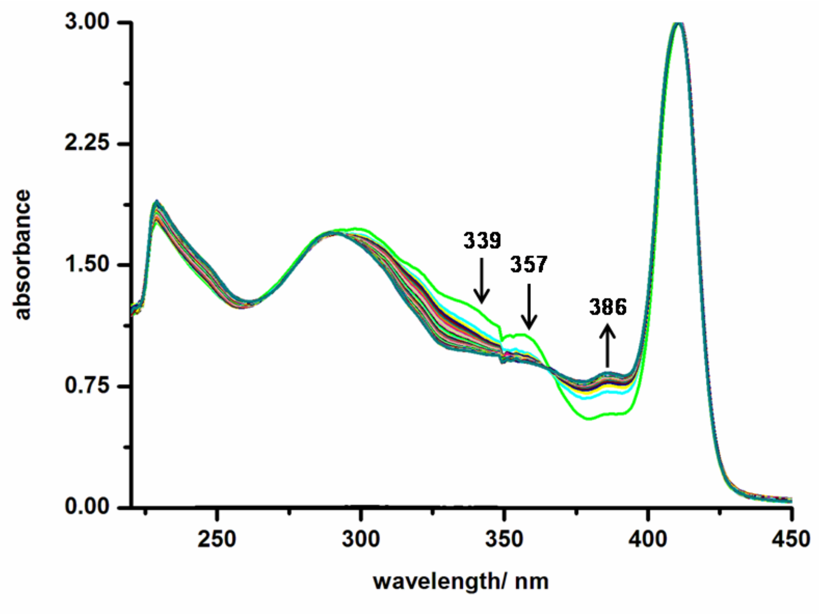


Figure S42. UV-Vis spectra for kinetics of conversion of NetState-I to NetState-II by addition of Zn^{2+} in CH_2Cl_2 at 298 K ($c = 10^{-6}$ M). After addition of Zn^{2+} to NetState-I spectra were recorded in 2 min intervals.

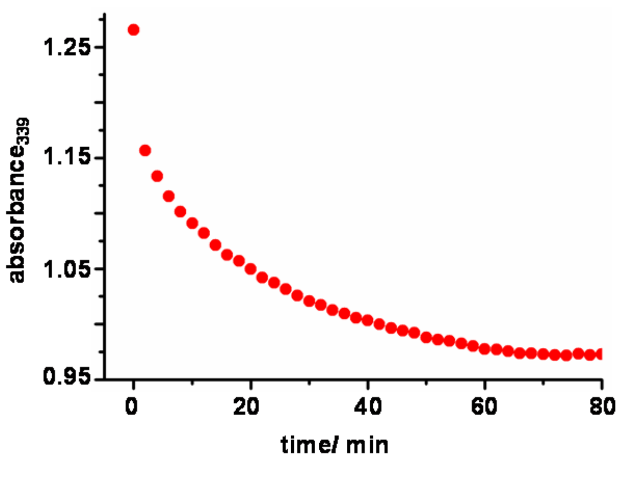


Figure S43. Changes in absorbance at 339 nm with time for conversion of NetState-I to NetState-II by addition of Zn^{2+} in CH_2Cl_2 at 298 K ($c = 10^{-6}$ M).

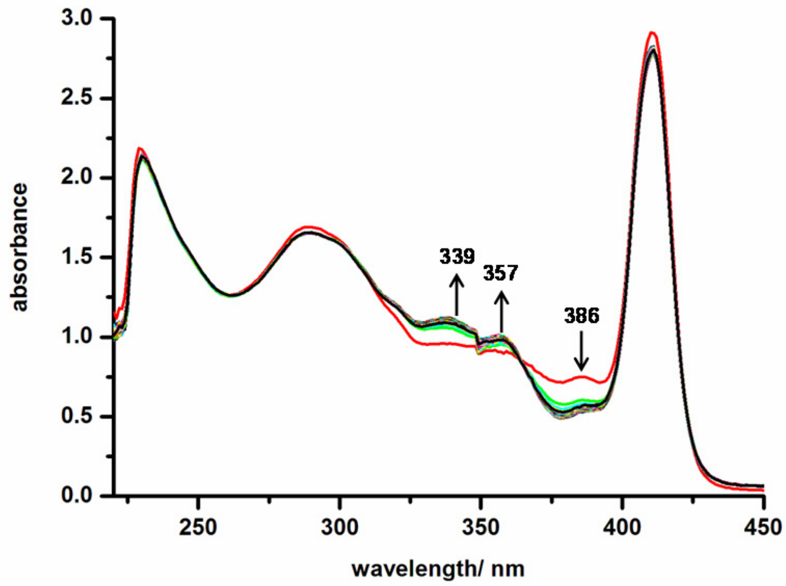


Figure S44. UV-Vis spectra after 30 s for kinetics of conversion of NetState-II to NetState-I by addition of hexacyclen in CH_2Cl_2 at 298 K (c = 10^{-6} M). After addition of hexacyclen to NetState-II spectra were recorded every 30 s for the first 10.5 min and then in 2 min intervals.

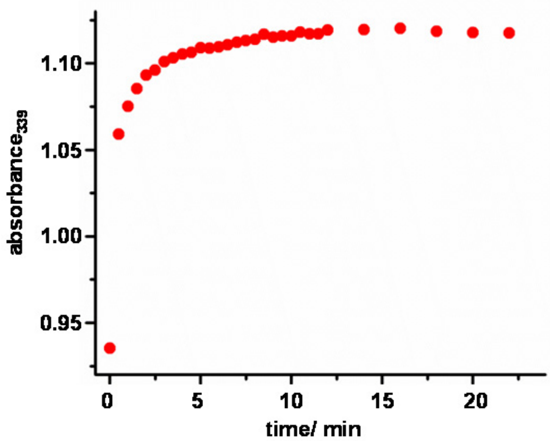


Figure S45. Changes in absorbance at 339 nm with time in the conversion of NetState-II to NetState-I upon addition of hexacyclen in CH_2Cl_2 at 298 K (c = 10^{-6} M).

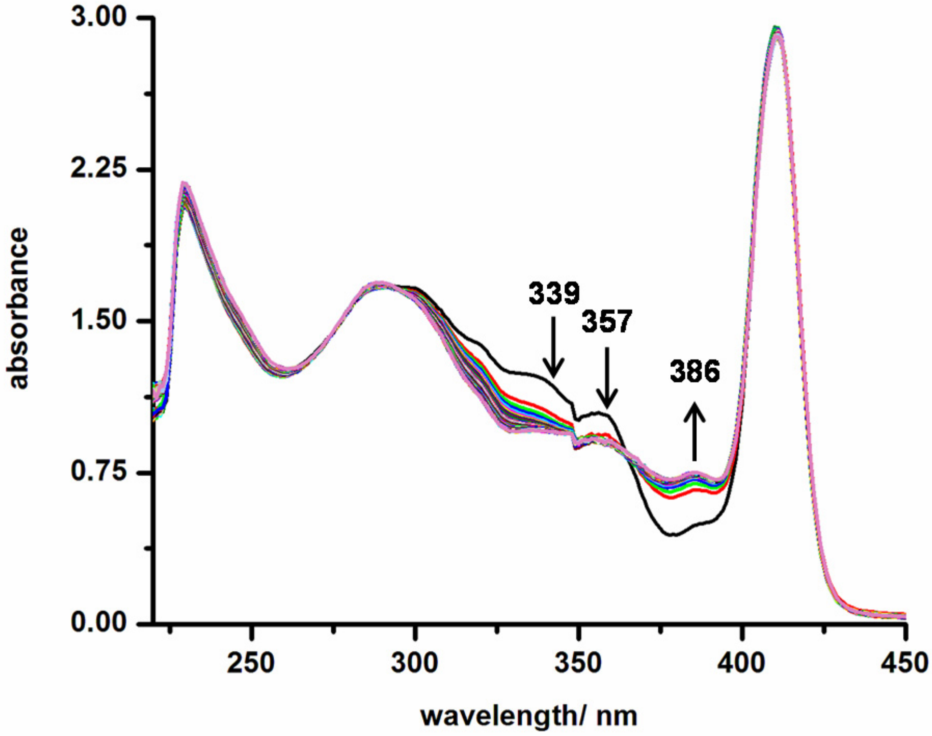


Figure S46. UV-Vis spectra for kinetics of conversion of NetState-I to NetState-II by addition of Zn^{2+} in presence of 3.0 equiv of iodide in CH_2Cl_2 at 298 K (c = 10^{-6} M). After addition of Zn^{2+} spectra were recorded every 30 s for the first 10.5 min and then in 2 min intervals.

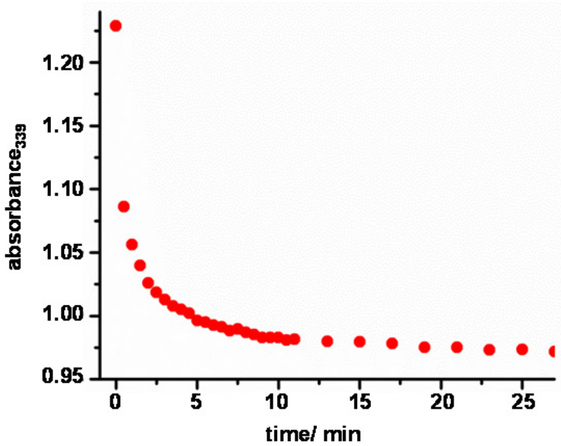


Figure S47. Changes in absorbance at 339 nm with time for conversion of NetState-I to NetState-II by addition of Zn^{2+} in presence of 3.0 equiv of iodide in CH_2Cl_2 at 298 K (c = 10^{-6} M).

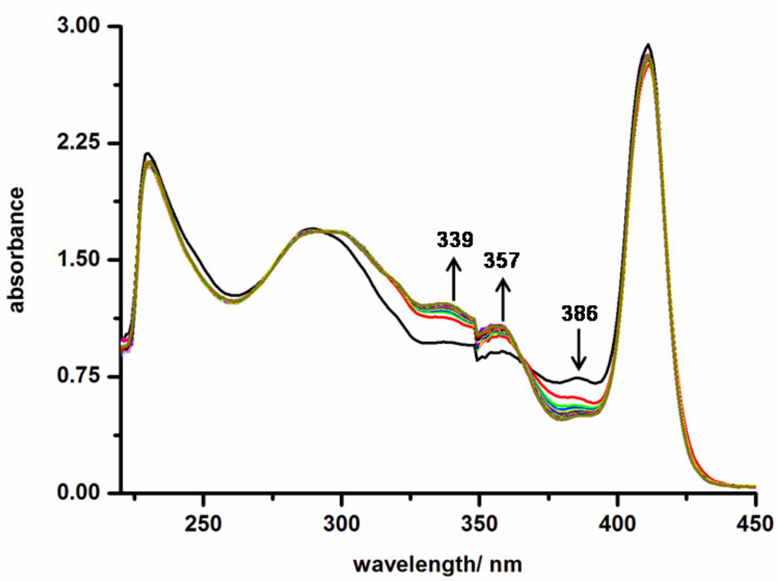


Figure S48. UV-Vis spectra for kinetics of conversion of NetState-II to NetState-I by addition of hexacyclen in presence of 3.0 equiv of iodide in CH_2Cl_2 at 298 K ($c = 10^{-6}$ M). After addition of hexacyclen spectra were recorded every 30 s for the first 10.5 min and then in 2 min intervals.

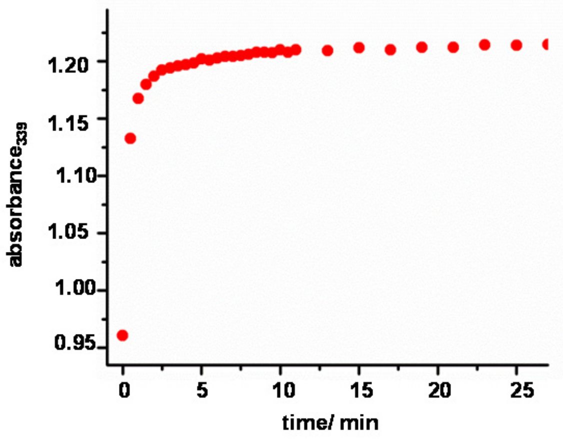


Figure S49. Changes in absorbance at 339 nm with time for conversion of NetState-II to NetState-I by addition of hexacyclen in presence of 3.0 equiv of iodide in CH_2Cl_2 at 298 K ($c = 10^{-6}$ M).

8. References

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