A Switchable Catalyst Duo for Acyl Transfer Proximity Catalysis and Regulation of Substrate Selectivity

Abir Goswami+, Sudhakar Gaikwad+, and Michael Schmittel*[a]
# Table of Contents

1. Synthesis ........................................................................................................ S2-S11
2. Synthesis and Characterization of Complexes ........................................... S12-S19
3. NMR Spectra .................................................................................................. S20-S43
4. $^1$H-$^1$H ROESY and Determination of Kinetic Parameters ............... S44
5. Catalytic Experiments ...................................................................................... S44-S54
6. ESI-MS Spectra ............................................................................................... S55-S62
7. UV-Vis spectra ................................................................................................ S62
8. Computational Studies ..................................................................................... S63-S69
9. References ......................................................................................................... S70
1. Synthesis

General Remarks

All solvents were dried by distillation prior to use while commercial reagents (6, 9, 16 A1, A2, B) were used without any further purification. Bruker Avance (400 MHz) and Jeol ECZ (500 MHz) spectrometers were taken to measure $^1$H and $^{13}$C NMR spectra using a deuterated solvent as the lock and residual protiated solvent as internal reference (CDCl$_3$: $\delta_H$ 7.26 ppm, $\delta_C$ 77.0 ppm; CD$_2$Cl$_2$: $\delta_H$ 5.32 ppm, $\delta_C$ 53.8 ppm, CD$_3$CN: $\delta_H$ 1.94 ppm, $\delta_C$ 1.3 ppm, 118.2 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, td = triplet of doublets, br = broad, m= multiplet. Coupling constant values are given in Hertz (Hz) and, wherever possible, assignment of protons is provided. The numbering of different carbons in different molecular skeletons does not necessarily follow IUPAC nomenclature rules; it was exclusively implemented for assigning NMR signals. All electrospray ionization (ESI-MS) spectra were recorded on a Thermo-Quest LCQ deca and theoretical isotopic distributions of the mass signals were calculated using IsoPro 3.0 software. Melting points of compounds were measured on a BÜCHI 510 instrument and are not corrected. Infrared spectra were recorded on a Perkin Elmer Spectrum Two FT-IR instrument. Elemental analysis was performed using the EA-3000 CHNS analyzer. UV-vis spectra were recorded on a Cary 100 UV/vis (298 K) spectrometer in quartz cuvettes. Binding constants were determined through UV-vis titrations in combination with a 1:1 binding formula of two ligands or with SPECFIT/32TM global analysis system by Spectrum Software Associates (Marlborough, MA). 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). The preparation of metal complexes was performed directly in the NMR tube using CD$_2$Cl$_2$ or CD$_2$Cl$_2$:CD$_3$CN as a solvent mixture. Compounds 5, 8, 10, 11, and 14 were synthesized according to literature known procedures.
Scheme 1. Synthesis of nanoswitch 1. Reaction conditions: (A) Pd(PPh₃)₄, DMF/Et₃N, 70 °C, 12 h, 58%. (B) Pd(PPh₃)₄, DMF/Et₃N, 70 °C, 20 h, 78%.

Scheme 2. Synthesis of ligand 3. Reaction conditions: (C) Pd(PPh₃)₄, benzene/Et₂NH (1:1), 70 °C, 16 h, 88%.

Scheme 3. Synthesis of ligand 2. Reaction conditions: (D) Pd(PPh₃)₄, THF/Et₃N, 80 °C, 18 h, 83%. (E) K₂CO₃, THF/MeOH, rt, 2 h, 89%. (F) Pd(PPh₃)₄, THF/Et₃N, 70 °C, 16 h, 64%. (G) Pd(PPh₃)₄, DMF/Et₃N, 80 °C, 18 h, 60%.
**4′-(4-(2-((3,5-Dibromophenyl)ethynyl)phenyl)ethynyl)phenyl)-2,2′:6′,2″-terpyridine (7)**

In a sealed tube, compounds 5 (500 mg, 1.15 mmol) and 6 (1.09 g, 3.46 mmol) were dissolved in 15 mL of DMF and 15 mL of Et3N. The reaction mixture was degassed three times by the freeze-pump-thaw method. Then, Pd(PPh3)4 (133 mg, 115 μmol) was added. After a further freeze-pump-thaw treatment, the mixture was allowed to stir at 70 °C for 12 h. All the solvents were then evaporated under vacuum. The crude product was worked up with dichloromethane (DCM) and ice-cold water. The organic part was dried over anhydrous Na2SO4. Finally, product 7 was purified by column chromatography using 10% ethyl acetate/DCM (Rf = 0.30, SiO2, 30% ethyl acetate /hexane) furnishing a colorless solid in 58% (445 mg, 0.667 mmol). **Mp. > 250 °C. IR (KBr):** ν = 825, 840, 752, 791, 863, 1034, 1249, 1381, 1464, 1491, 1516, 1567, 1585, 2027, 2157, 2218, 2311, 2853, 2924, 2951 cm⁻¹. **1H NMR (CDCl₃, 400 MHz):** δ = 7.33-7.40 (m, 4H, [b+i+j]-H), 7.54–7.58 (m, 1H, k/h-H), 7.59–7.63 (m, 1H, h/k-H), 7.65 (d, 4J = 1.8 Hz, 2H, m-H), 7.66 (t, 4J = 1.8 Hz, 1H, n-H), 7.71 (d, 3J = 8.4 Hz, 2H, g-H), 7.89 (td, 3J = 8.0 Hz, 4J = 1.6 Hz, 2H, c-H), 7.94 (d, 3J = 8.4 Hz, 2H, f-H), 8.69 (ddd, 3J = 8.0 Hz, 4J = 1.6 Hz, 5J = 0.8 Hz, 2H, d-H), 8.74 (ddd, 3J = 4.8 Hz, 4J = 1.6 Hz, 5J = 0.8 Hz, 2H, a-H), 8.76 (s, 2H, e-H) ppm. **13C NMR (CDCl₃, 100 MHz):** δ = 88.9, 90.1, 90.3, 93.1, 118.2, 120.8, 122.2, 123.1, 123.3, 124.4, 125.5, 126.1, 126.9, 127.7, 128.2, 131.3, 131.3, 131.6, 132.4, 133.5, 136.3, 138.1, 148.6, 148.8, 155.5, 155.6 ppm. **Elemental analysis:** Anal. Calcd for C₃₇H₂₁Br₂N₃•H₂O: C, 64.84; H, 3.38; N, 6.13. Found: C, 65.07; H, 2.99; N, 5.85. **ESI-MS:** m/z (%) 668.5 (100) [15+H]+.
Synthesis of ligand 1

In a sealed tube compounds 7 (200 mg, 300 μmol) and 8 (409 mg, 900 μmol) were dissolved in 15 mL of DMF and 15 mL of Et₃N. The reaction mixture was degassed three times by the freeze-pump-thaw method. Then, Pd(PPh₃)₄ (70.0 mg, 60.0 μmol) was added. After a further freeze-pump-thaw treatment, the mixture was allowed to stir at 70 °C for 20 h. All the solvents were then evaporated under vacuum. The crude product was worked up with DCM and ice-cold water. The organic part was dried over anhydrous Na₂SO₄. Finally, product 1 was afforded as a colorless solid after column chromatography using 30% ethyl acetate/hexane (Rᵣ = 0.30, SiO₂, 30% ethyl acetate /hexane) in a yield of 78% (331 mg, 234 μmol). Mp. > 250 ºC. IR (KBr): ν = 663, 827, 845, 758, 792, 853, 1035, 1249, 1384, 1468, 1493, 1514, 1567, 1585, 2027, 2157, 2219, 2310, 2853, 2924, 2957 cm⁻¹. ¹H-NMR (400 MHz, CD₂Cl₂): δ = 1.82 (s, 12H, 13-H), 2.04 (s, 12H, 10-H), 2.32 (s, 6H, 11-H), 2.51 (s, 12H, 12-H), 6.94 (s, 4H, 9-H), 7.28 (ddd, 3J = 7.6, 3J = 4.8 Hz, 4J = 1.2 Hz, 2H, b-H), 7.40-7.43 (m, 2H, [i+j]-H), 7.44 (d, 3J = 8.2 Hz, 2H, 8/3-H), 7.55 (d, 3J = 8.2 Hz, 2H, 3/8-H), 7.65-7.69 (m, 2H, [h+k]-H), 7.83-7.79 (m, 7H, [c+m+n+f/g]-H), 7.88 (s, 4H, [5+6]-H), 7.97 (d, 3J = 8.6 Hz, 2H, g/f-H), 8.27 (d, 3J = 8.2 Hz, 2H, 7/4-H), 8.32 (d, 3J = 8.2 Hz, 2H, 4/7-H), 8.66-8.63 (m, 4H, [a+d]-H), 8.79 (s, 2H, e-H) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz): δ = 17.6, 18.6, 20.4, 21.2, 89.6, 90.0, 90.7, 92.7, 93.6, 95.6, 118.6, 121.3, 122.6, 124.2, 124.3 (2C), 124.7, 124.9, 125.4, 125.8, 126.2, 126.5 (2C), 126.6, 127.5, 127.6, 127.7, 128.6, 128.7, 128.9, 132.1, 132.2, 132.3, 132.8, 133.8, 134.0, 136.0, 136.3, 136.7, 137.0, 137.7, 138.5, 138.7, 142.1, 146.6 (2C), 149.1, 149.5, 156.2, 156.4, 160.5, 161.3 ppm. Elemental analysis: Anal. Calcd for C₁₀₃H₇₉N₇: C, 87.44; H, 5.63; N, 6.93. Found: C, 87.52; H, 5.27; N, 6.75. ESI-MS: m/z (%) = 1415.0 (10) [(1+H)]⁺, 708.8 (100) [(1+2H)]²⁺.
Synthesis of ligand 3

A mixture of compound 8 (180 mg, 0.396 mmol) and 1,3-diodobenzene (9, 50.0 mg, 0.152 mmol) was placed in a sealed tube. The tube was evacuated and filled with nitrogen (3×) and pre-degassed dry Et₂NH/benzene (50 mL, 1:1, v/v) was added. Thereafter, Pd(PPh₃)₄ (20.0 mg, 17.3 μmol) was added under N₂ and the mixture was allowed to stir at 70 °C for 16 h. After evaporation of the solvent, the residue was extracted in DCM (100 mL) and washed with deionized water (150 mL). The organic layer was dried over anhydrous Na₂SO₄ and the solvent was removed in vacuo. The crude product was subjected to column chromatography on silica gel using 10% EtOAc in n-hexane (Rf = 0.3, SiO₂, 30% EtOAc in n-hexane) to yield ligand 3 as a white solid (131 mg, 0.133 mmol, 88%). Mp: > 250 °C. IR (KBr): ν~ = 410, 503, 627, 828, 901, 954, 1004, 1064, 1171, 1264, 1398, 1484, 1583, 1618, 1784, 2221, 2312, 2791, 2982 cm⁻¹. ¹H NMR (CD₂Cl₂, 400 MHz, 298 K): δ = 1.95 (s, 12H, 13-H), 2.05 (s, 12H, 10-H), 2.34 (s, 6H, 11-H), 2.56 (s, 12H, 12-H), 6.96 (s, 4H, 9-H), 7.41 (td, ³J = 8.0 Hz, ⁵J = 1.0 Hz, 1H, 15-H), 7.55 (d, ³J = 8.0 Hz, 2H, 3/8-H), 7.56 (d, ³J = 8.0 Hz, 2H, 8/3-H), 7.57 (dd, ³J = 8.0 Hz, ⁴J = 1.6 Hz, 2H, 14-H), 7.81 (td, ³J = 1.6 Hz, ⁵J = 1.0 Hz, 1H, 16-H), 7.91 (s, 4H, 5+6-H), 8.34 (d, ³J = 8.0 Hz, 2H, 4/7-H), 8.36 (d, ³J = 8.0 Hz, 2H, 7/4-H) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz, 298 K): δ = 17.7, 18.6, 20.5, 21.3, 89.9, 96.4, 123.0, 124.8 (2C), 125.0, 126.5, 126.7, 127.7 (2C), 128.6, 128.6, 129.0, 131.2, 132.3, 134.2, 136.1, 136.4, 136.5, 136.7, 137.8, 138.6, 142.1, 146.7, 160.6, 161.5 ppm. ESI-MS: m/z (%) = 984.4 (100) [(3+H)]⁺, 492.9 (35) [(3+2H)]²⁺. Elemental analysis: Anal. Calcd for C₇₂H₆₂N₄•H₂O: C, 86.36; H, 6.44; N, 5.60. Found: C, 86.77; H, 6.23; N, 5.52.
Synthesis of ligand 12

A solution of compounds 10 (180 mg, 603 µmol) and 11 (160 mg, 513 µmol) in anhydrous Et₃N (20 mL) and THF (20 mL) was degassed using the freeze-pump-thaw procedure (3×). Pd(PPh₃)₄ (50.0 mg, 43.3 µmol) was added and the reaction mixture heated to 80 °C for 18 h (TLC). After evaporation of the solvents, deionized water (50 mL) was added and the residue was extracted in DCM (50 mL). The organic layer was dried over anhydrous Na₂SO₄ and evaporated. The yellow residue was subjected to column chromatography on silica gel using gradient elution, 20% to 40% EtOAc in n-hexane (Rₛ = 0.3, SiO₂, 50% EtOAc in DCM). Compound 12 was afforded as pale yellow solid (226 mg, 427 µmol, 83%). Mp: 163 ºC. IR (KBr): ν = 523, 621, 826, 911, 973, 1024, 1077, 1152, 1254, 1376, 1461, 1524, 1781, 2219, 2316, 2745, 2815, 2995 cm⁻¹. ¹H NMR (CD₂Cl₂, 400 MHz, 298 K): δ = 0.29 (s, 9H, TMS-H), 7.30–7.35 (m, 2H, [n+o]-H), 7.37 (ddd, ³J = 8.0 Hz, ⁴J = 4.8 Hz, ⁷J = 1.8 Hz, 1H, b-H), 7.51–7.57 (m, 2H, m+p-H), 7.57–7.62 (m, 4H, [k+l]-H), 7.89 (td, ³J = 8.0 Hz, ⁴J = 1.2 Hz, 1H, c-H), 7.99 (t, ³J = 8.0 Hz, 1H, f-H), 8.01 (dd, ³J = 8.2 Hz, ⁴J = 2.0 Hz, 1H, i-H), 8.48 (d, ³J = 8.0 Hz, 1H, e/g-H), 8.49 (d, ³J = 8.0 Hz, 1H, g/e -H), 8.64 (ddd, ³J = 8.0 Hz, ⁴J = 1.8 Hz, ⁷J = 0.8 Hz, 1H, d-H), 8.67 (dd, ³J = 8.2 Hz, ⁵J = 0.8 Hz, 1H, h-H), 8.70 (ddd, ³J = 4.8 Hz, ⁴J = 1.2 Hz, ⁵J = 0.8 Hz, 1H, a-H), 8.85 (dd, ⁴J = 2.0 Hz, ⁵J = 0.8 Hz, 1H, j-H) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz, 298 K): δ = 0.1, 88.8, 90.6, 93.2, 93.3, 99.3, 103.5, 120.4, 120.6, 121.3, 121.5(2C), 123.0, 124.0, 124.3, 125.9, 126.0, 128.7, 128.8, 132.1 (2C), 132.2, 132.7, 137.2, 138.3, 139.6, 149.6, 152.0, 155.0, 155.5, 155.9, 156.3. ESI-MS: m/z (%) = 530.4 (100) [12+H]⁺. Elemental analysis: Anal. Calcd for C₃₆H₂₇N₃Si: C, 81.63; H, 5.14; N, 7.93. Found: C, 81.54; H, 5.32; N, 7.78.
Synthesis of ligand 13

Compound 12 (130 mg, 245 µmol) was dissolved in a solution of THF and MeOH (90 mL, 2:1, v/v). Then an aq. solution of K₂CO₃ (340 mg, 2.46 mmol, in 5 mL of deionized water) was added and the reaction mixture was stirred at room temperature for 2 h (TLC). After removal of the solvent, water was added and the residue was extracted in DCM (25 mL). After evaporation of the solvents, the crude solid was purified by column chromatography on silica gel using 40% EtOAc in n-hexane (Rᶠ = 0.3, SiO₂, 60% EtOAc/DCM) to afford compound 13 as yellow solid (100 mg, 219 µmol, 89%). Mp: 170 ºC. IR (KBr): ν = 416, 527, 632, 815, 941, 1035, 1067, 1179, 1261, 1382, 1474, 1588, 1619, 2219, 2726, 2976 cm⁻¹.

¹H NMR (CDCl₃, 400 MHz, 298 K): δ = 3.40 (s, 1H, q-H), 7.29–7.36 (m, 2H, [n+o]-H), 7.54–7.57 (m, 2H, [m+p]-H), 7.57–7.60 (m, 4H, [k+l]-H), 7.91 (td, ³J = 8.0 Hz, ⁴J = 1.2 Hz, 1H, c-H), 7.98 (t, ³J = 8.0 Hz, 1H, f-H), 8.01 (dd, ³J = 8.2 Hz, ⁴J = 2.0 Hz, 1H, i-H), 8.49 (d, ³J = 8.0 Hz, 1H, e/g-H), 8.50 (d, ³J = 8.0 Hz, 1H, g/e -H), 8.63 (dd, ³J = 8.0 Hz, ⁴J = 1.8 Hz, ⁵J = 0.8 Hz, 1H, d-H), 8.66 (dd, ³J = 8.2 Hz, ⁵J = 0.8 Hz, 1H, h-H), 8.74 (ddd, ³J = 4.8 Hz, ⁴J = 1.2 Hz, ⁵J = 0.8 Hz, 1H, a-H), 8.85 (dd, ³J = 2.0 Hz, ⁵J = 0.8 Hz, 1H, j-H) ppm. ¹³C NMR (CDCl₃, 100 MHz, 298 K): δ = 81.3, 82.1, 88.3, 90.0, 93.0, 93.2, 120.1, 120.5, 121.4 (2C), 121.5, 122.6, 123.6, 124.0, 124.7, 126.0, 128.2, 128.6, 131.6, 131.8 (2C), 132.7, 137.3, 138.1, 139.3, 148.8, 151.6 (2C), 154.7, 155.0, 155.8 ppm. ESI-MS: m/z (%) = 458.4 (100) [13+H]+. Elemental analysis: Anal. Calcd for C₃₃H₁₉N₃•1.5H₂O: C, 81.80; H, 4.58; N, 8.67. Found: C, 81.84; H, 4.34; N, 8.62.
Synthesis of ligand 15

A solution of terpyridine derivative 13 (90.0 mg, 197 µmol) and trimethyl((4-(tris(4-bromo-phenyl)methyl)phenyl)ethynyl)silane (14, 500 mg, 765 µmol) in a mixture of distilled anhydrous THF (20 mL) and Et₃N (20 mL) was subjected to freeze-pump-thaw cycles (3×). After addition of Pd(PPh₃)₄ (50 mg, 43.3 µmol), the resultant mixture was heated to 70 °C for 16 h (TLC). The reaction was allowed to cool to 25 °C and the solvents were removed in vacuo. The crude product was extracted in DCM (50 mL), then washed with deionized water (60 mL × 2) and a saturated brine solution (30 mL). The organic layer was dried over anhydrous MgSO₄ and evaporated. The crude product was purified by column chromatography on neutral Al₂O₃ using 10% EtOAc in n-hexane as an eluent (Rf = 0.3, neutral Al₂O₃, 30% EtOAc in n-hexane) furnishing the target compound 15 as off colorless solid (130 mg, 126 µmol, 64%). Mp: > 250 ºC.

IR (KBr): ν = 414, 537, 672, 842, 971, 1071, 1093, 1156, 1243, 1355, 1442, 1565, 1789, 2217, 2788, 2821, 2945 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz, 298 K): δ = 0.23 (s, 9H, TMS-H), 7.03 (d, ³J = 8.0 Hz, 4H, s/t-H), 7.11 (d, ³J = 8.0 Hz, 2H, u/r-H), 7.14 (d, ³J = 8.0 Hz, 2H, t/u-H), 7.32–7.35 (m, 2H, [n+o]-H), 7.35 (ddd, ³J = 8.0 Hz, ³J = 4.8 Hz, ⁴J = 1.8 Hz, 1H, b-H), 7.38 (d, ³J = 8.0 Hz, 2H, q/v-H), 7.40 (d, ³J = 8.0 Hz, 4H, t/s-H), 7.46 (d, ³J = 8.0 Hz, 2H, v/q-H), 7.52–7.55 (m, 4H, [k+l]-H), 7.56–7.59 (m, 2H, [m+p]-H), 7.88 (td, ³J = 8.0 Hz, ⁴J = 1.2 Hz, 1H, c-H), 7.98 (t, ³J = 8.0 Hz, 1H, f-H), 7.99 (dd, ³J = 8.2 Hz, ⁴J = 2.0 Hz, 1H, i-H), 8.47 (d, ³J = 8.0 Hz, 1H, e/g-H), 8.49 (d, ³J = 8.0 Hz, 1H, g/e-H), 8.63 (ddd, ³J = 8.0 Hz, ⁴J = 1.8 Hz, ²J = 0.8 Hz, 1H, d-H), 8.66 (dd, ³J = 8.2 Hz, ⁵J = 0.8 Hz, 1H, h-H), 8.72 (ddd, ³J = 4.8 Hz, ⁴J = 1.2 Hz, ²J = 0.8 Hz, 1H, a-H), 8.85 (dd, ⁴J = 2.0 Hz, ⁵J = 0.8 Hz, 1H, j-H) ppm. ¹³C NMR (CDCl₃, 100 MHz, 298 K): δ = −0.1, 64.3,
88.5, 88.8, 90.5, 93.1 (2C), 95.0, 93.2, 104.5, 120.0, 120.4, 120.7, 121.2, 121.3 (2C), 121.4, 121.5, 122.6, 123.6, 123.8, 125.4, 125.7, 128.2, 128.3, 130.6, 130.8, 131.0, 131.2, 131.5, 131.6, 131.7, 131.9, 132.0, 132.5, 136.9, 138.0, 139.3, 144.6, 145.8, 145.9, 149.2, 151.7, 154.6, 155.1, 155.5, 156.1. **ESI-MS:** m/z (%) = 1030.2 (100) [15+H]⁺. **Elemental analysis:** Anal. Calcd for C₆₃H₄₃Br₂N₃Si: 73.47; H, 4.21; N, 4.08. Found: C, 73.48; H, 4.17; N, 3.80.

**Synthesis of ligand 2**

A solution of compound 15 (70.0 mg, 68.0 µmol) and 2-(4-ethynyl-2,3,5,6-tetramethylphenyl)-9-mesityl-[1,10]-phenanthroline (8, 130 mg, 286 µmol) in a mixture of freshly distilled anhydrous DMF and Et₃N (40 mL, 1:1, v/v) was degassed using freeze-pump-thaw cycles (3×). After addition of Pd(PPh₃)₄ (20.0 mg, 17.3 µmol), the resulting mixture was heated to 80 °C for 18 h (TLC). The reaction mixture was allowed to cool to room temperature and the solvent was evaporated in vacuo. The residue was dissolved in DCM (25 mL), and sequentially washed with deionized water (25 mL × 2) and a saturated brine solution (50 mL × 2). The organic layer was removed and the aqueous layer was re-extracted in DCM (25 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and evaporated. The chromatographic purification of the crude residue using 10% EtOAc in DCM (Rf = 0.3, SiO₂, 30% EtOAc in DCM) afforded the title compound 2 as off colorless solid (73.0 mg, 41.1 µmol, 60%). **Mp:** > 250 °C. **IR (KBr):** \( \tilde{\nu} \) = 417, 631, 742, 853, 907, 1051, 1046, 1179, 1265, 1392, 1481, 1548, 1619, 1743, 2220, 2317, 2783, 2962 cm⁻¹. **¹H NMR (CD₂Cl₂, 400 MHz, 298 K):** \( \delta \) = 0.23 (s, 9H, TMS-H), 1.90 (s, 12H, 13-H), 2.02 (s, 12H, 10-H), 2.31 (s, 6H, 11-H), 2.85 (s, 9H, TMS-H), 3.15 (s, 12H, 11-H), 3.20 (s, 12H, 12-H), 4.50 (s, 18H, 13-H), 5.20 (s, 18H, 10-H), 5.30 (s, 18H, 7-H), 5.50 (s, 18H, 11-H), 5.80 (s, 18H, 12-H), 6.00 (s, 18H, 7-H), 6.20 (s, 18H, 8-H), 6.30 (s, 18H, 9-H), 6.60 (s, 18H, 6-H), 6.80 (s, 18H, 5-H), 6.90 (s, 18H, 10-H), 7.00 (s, 18H, 11-H), 7.10 (s, 18H, 12-H), 7.20 (s, 18H, 13-H).
2.50 (s, 12H, 12-H), 6.93 (s, 4H, 9-H), 7.25 (d, 3J = 8.0 Hz, 2H, u/t-H), 7.27 (d, 3J = 8.0 Hz, 4H, s/t-H), 7.28 (ddd, 3J = 8.0 Hz, 3J = 4.8 Hz, 4J = 1.8 Hz, 1H, b-H), 7.29 (d, 3J = 8.0 Hz, 2H, t/u-H), 7.36–7.38 (m, 2H, n+o-H), 7.42 (d, 3J = 8.0 Hz, 2H, v/q-H), 7.50 (d, 3J = 8.0 Hz, 2H, 8/3-H), 7.52 (d, 3J = 8.0 Hz, 2H, q/v-H), 7.53 (d, 3J = 8.0 Hz, 4H, t/s-H), 7.54 (d, 3J = 8.0 Hz, 2H, 3/8-H), 7.54–7.57 (m, 4H, k+l-H), 7.57–7.60 (m, 2H, m+p-H), 7.80 (td, 3J = 8.0 Hz, 4J = 1.2 Hz 1H, c-H), 7.89 (s, 4H, 5+6-H), 7.94 (t, 3J = 8.0 Hz, 1H, f-H), 7.99 (dd, 3J = 8.2 Hz, 4J = 2.0 Hz, 1H, i-H), 8.30 (d, 3J = 8.0 Hz, 2H, 4/7-H), 8.32 (d, 3J = 8.0 Hz, 2H, 7/4-H), 8.45 (d, 3J = 8.0 Hz, 1H, e/g-H), 8.47 (d, 3J = 8.0 Hz, 1H, g/e-H), 8.63 (ddd, 3J = 8.0 Hz, 4J = 1.8 Hz, 5J = 0.8 Hz, 1H, d-H), 8.66 (dd, 3J = 8.2 Hz, 5J = 0.8 Hz, 1H, h-H), 8.72 (ddd, 3J = 4.8 Hz, 4J = 1.2 Hz, 5J = 0.8 Hz, 1H, a-H), 8.84 (dd, 4J = 2.0 Hz, 5J = 0.8 Hz, 1H, j-H) ppm.

13C NMR (CD2Cl2, 100 MHz, 298 K): δ = −0.1, 17.7, 18.5, 20.4, 21.2, 65.3, 88.8 (2C), 89.7, 90.7, 93.3, 93.4, 93.8, 95.0, 96.8, 105.0, 120.4, 120.6, 121.3, 121.5 (2C), 121.6, 122.5, 123.1 (2C), 123.9, 124.2, 124.8, 125.0, 125.7, 126.1, 126.5, 126.6, 127.6, 127.7, 128.6 (2C), 128.8, 131.2, 131.3 (2C), 131.4, 131.5, 131.7, 132.0, 132.1 (2C), 132.3 (2C), 133.1, 136.1, 136.4 (2C), 136.5, 137.2, 137.8, 138.2, 138.4, 139.6, 141.9, 146.0, 146.6 (2C), 146.7, 146.9, 149.5, 152.0, 155.0, 155.3, 155.8, 156.3, 160.5, 161.4 ppm. ESI-MS: m/z (%) = 1777.6 (100) [2+H]+, 889.4 (100) [2+2H]2+. Elemental analysis: Anal. Calcd for C129H101N7Si•H2O: C, 86.30; H, 5.78; N, 5.46. Found: C, 86.39; H, 5.87; N, 5.52.
2. Synthesis and Characterization of Complexes

Copper complex [Cu(1)]^+

In an NMR tube, nanoswitch 1 (0.70 mg, 0.49 µmol) and [Cu(CH$_3$CN)$_4$]PF$_6$ (0.18 mg, 0.49 µmol) were mixed in deuterated DCM (400 µL). Then, the proton NMR spectrum was recorded without any further purification. Yield: quantitative. Mp: > 250 °C. IR (KBr): ν = 536, 620, 905, 954, 1012, 1064, 1141, 1264, 1378, 1464, 1581, 1614, 2233, 2314, 2791, 2851, 2882 cm$^{-1}$. $^1$H-NMR (500 MHz, CD$_2$Cl$_2$, 298 K):

δ = 1.35 (s, 6H, 13-H), 1.61 (s, 6H, 10-H), 1.79 (s, 6H, 13u-H), 1.91 (s, 3H, 11-H), 1.96 (s, 6H, 12-H), 2.04 (s, 6H, 10u-H), 2.33 (s, 3H, 11u-H), 2.56 (s, 6H, 12u-H), 6.41 (s, 2H, 9-H), 6.96 (s, 2H, 9u-H), 7.12 (ddd, $^3$J = 8.0 Hz, $^3$J = 5.4 Hz, $^4$J = 0.8 Hz, 2H, b-H), 7.42-7.45 (m, 2H, i+j-H), 7.43 (t, $^4$J = 1.6 Hz, 1H, m-H), 7.54 (d, $^3$J = 8.2 Hz, 1H, 8u/3u-H), 7.56 (d, $^3$J = 8.2 Hz, 1H, 3u/8u-H), 7.58 (t, $^4$J = 1.6 Hz, 1H, l-H), 7.60 (td, $^3$J = 8.0 Hz, $^4$J = 1.2 Hz, 2H, c-H), 7.64 (d, $^3$J = 8.2 Hz, 1H, 8/3-H), 7.64-7.67 (m, 2H, h+k-H), 7.68 (dd, $^3$J = 5.4 Hz, $^4$J = 1.2 Hz, 2H, a-H), 7.78 (t, $^4$J = 1.6 Hz, 1H, n-H), 7.89 (d, $^3$J = 8.6 Hz, 2H, g/f -H), 7.91 (d, $^3$J = 8.2 Hz, 1H, 3/8-H), 7.92 (s, 2H, 5u+6u-H), 7.98 (dd, $^3$J = 8.0 Hz, $^4$J = 0.8 Hz, 2H, d-H), 8.04 (d, $^3$J = 8.6 Hz, 2H, f/g -H), 8.21 (d, $^3$J = 8.6 Hz, 1H, 6/5-H), 8.27 (d, $^3$J = 8.6 Hz, 1H, 5/6-H), 8.30 (s, 2H, e-H), 8.35 (d, $^3$J = 8.2 Hz, 1H, 7u/4u-H), 8.37 (d, $^3$J = 8.2 Hz, 1H, 4u/7u-H), 8.57 (d, $^3$J = 8.2 Hz, 1H, 7/4-H), 8.73 (d, $^3$J = 8.2 Hz, 1H, 4/7-H) ppm. ESI-MS: m/z (%) = 1478.0 (100) [Cu(1)]^+. **Elemental analysis:** Anal. Calcd for C$_{103}$H$_{79}$CuF$_6$N$_7$P•CH$_2$Cl$_2$: C, 73.12; H, 4.78; N, 5.74 Found: C, 73.15; H, 4.47; N, 6.07.
Copper rotor complex \([\text{Cu}_2(1)]^{2+}\)

In an NMR tube, complex \([\text{Cu}(1)]^+\) (0.64 mg, 0.45 µmol) and \([\text{Cu(CH}_3\text{CN})_4]\text{PF}_6\) (0.34 mg, 0.90 µmol) were mixed in CD\(_2\)Cl\(_2\) (400 µL), and the NMR spectrum was recorded without further purification. Yield: quantitative. **Mp:** > 250 ºC. **IR (KBr):** \(\nu \approx 535, 628, 858, 984, 1062, 1271, 1294, 1391, 1581, 2217, 2317, 2791, 2813, 2982\) cm\(^{-1}\). **\(^1\)H-NMR (500 MHz, CD\(_2\)Cl\(_2\), 298 K):** \(\delta = 1.30\) (s, 6H, 13-\(H\)), 1.73 (s, 6H, 10-\(H\)), 1.83 (s, 3H, 11-\(H\)), 1.86 (s, 6H, 12-\(H\)), 1.98 (s, 6H, 13c-\(H\)), 2.02 (s, 6H, 10c-\(H\)), 2.34 (s, 3H, 11c-\(H\)), 2.52 (s, 6H, 12c-\(H\)), 6.38 (s, 2H, 9-\(H\)), 6.97 (s, 2H, 9c-\(H\)), 7.11 (ddd, \(^3J = 8.0\) Hz, \(^4J = 4.8\) Hz, \(^4J = 1.2\) Hz, 2H, b-\(H\)), 7.26–7.43 (m, 3H, [i+j+m]-\(H\)), 7.52–7.64 (m, 2H, [h+k]-\(H\)), 7.59 (t, \(^4J = 1.2\) Hz, 1H, l/n-\(H\)), 7.61 (td, \(^3J = 8.0\) Hz, \(^4J = 1.2\) Hz, 2H, c-\(H\)), 7.64 (d, \(^3J = 8.4\) Hz, 1H, 8/3-\(H\)), 7.69 (dd, \(^3J = 4.8\) Hz, \(^4J = 1.2\) Hz, 2H, a-\(H\)), 7.75 (t, \(^4J = 1.2\) Hz, 1H, n/l-\(H\)), 7.86 (d, \(^3J = 8.4\) Hz, 2H, f/g-\(H\)), 7.89 (d, \(^3J = 8.4\) Hz, 1H, 3/8-\(H\)), 7.91 (d, \(^3J = 8.4\) Hz, 1H, 8c/3c-\(H\)), 7.93 (d, \(^3J = 8.4\) Hz, 1H, 3c/8c-\(H\)), 8.00 (dd, \(^3J = 8.0\) Hz, \(^4J = 1.2\) Hz, 2H, d-\(H\)), 8.05 (d, \(^3J = 8.4\) Hz, 2H, g/f-\(H\)), 8.16 (s, 2H, [5c+6c]-\(H\)), 8.21 (d, \(^3J = 8.8\) Hz, 1H, 6/5-\(H\)), 8.26 (d, \(^3J = 8.8\) Hz, 1H, 5/6-\(H\)), 8.30 (s, 2H, e-\(H\)), 8.57 (d, \(^3J = 8.4\) Hz, 1H, 7/4-\(H\)), 8.68 (d, \(^3J = 8.4\) Hz, 1H, 7c/4c-\(H\)), 8.71 (d, \(^3J = 8.4\) Hz, 1H, 4c/7c-\(H\)), 8.73 (d, \(^3J = 8.4\) Hz, 1H, 4/7-\(H\)) ppm. **ESI-MS:** \(m/z\) (%) = 1478.0 (10) \([\text{Cu}(1)]^+\), 770.1 (100) \([\text{Cu}_2(1)]^{2+}\). **Elemental analysis:** Anal. Calcd for C\(_{103}\)H\(_{79}\)Cu\(_2\)F\(_{12}\)N\(_7\)P\(_2\): C, 67.53; H, 4.35; N, 5.35. Found: C, 67.23; H, 4.62; N, 4.96.
Synthesis of complex $[\text{Fe}(1)_2]^{2+}$

To a solution of nanoswitch 1 (560 µg, 0.396 µmol) in CD$_2$Cl$_2$, a standard solution of Fe(BF$_4$)$_2$$\cdot$6H$_2$O (66.8 µg, 0.198 µmol) in CD$_3$CN was transferred. Subsequently, $^1$H NMR was measured without further purification. Yield: Quantitative. **Mp:** > 250 ºC. **IR (KBr):** $\tilde{\nu}$ = 621, 808, 958, 1044, 1094, 1271, 1284, 1318, 1584, 1784, 2217, 2315, 2793, 2962 cm$^{-1}$. $^1$H-NMR (400 MHz, CD$_3$CN:CD$_2$Cl$_2$, 1:5, 298 K): $\delta$ = 1.87 (s, 24H, 13-H), 1.95 (s, 24H, 10-H), 2.24 (s, 12H, 11-H), 2.57 (s, 24H, 12-H), 6.87 (s, 8H, 9-H), 6.94 (dd, $^3J = 8.0, 4.8$ Hz, 4H, b-H), 6.95 (d, $^3J = 4.8$ Hz, 4H, a-H), 7.38 (d, $^3J = 8.4$ Hz, 4H, 3/8-H), 7.46-7.48 (m, 4H, [i+j]-H), 7.52 (d, $^3J = 8.4$ Hz, 4H, 8/3-H), 7.68-7.74 (m, 8H, [h+k+c]-H), 7.84 (t, $^4J = 1.2$ Hz, 2H, n-H), 7.86 (t, $^4J = 1.2$ Hz, 4H, m+1-H), 7.87 (d, $^3J = 8.8$ Hz, 4H, 5/6-H), 7.89 (d, $^3J = 8.8$ Hz, 4H, 6/5-H), 8.01 (d, $^3J = 8.4$ Hz, 4H, g/f-H), 8.27 (d, $^3J = 8.4$ Hz, 4H, f/g-H), 8.30 (d, $^3J = 8.4$ Hz, 4H, 7/4-H), 8.32 (d, $^3J = 8.4$ Hz, 4H, 7/4-H), 8.34 (d, $^3J = 8.0$ Hz, 4H, d-H), 9.01 (s, 4H, e-H) ppm. **ESI-MS:** m/z (%) = 1443.2 (100) [Fe(1)$_2$]$^{2+}$, 1415.0 (15) [1+H]$^+$, 708.0 (12) [1+2H]$^{2+}$. **Elemental analysis:** Anal. Calcd for C$_{206}$H$_{158}$BF$_4$FeN$_{14}$$\cdot$3CH$_2$Cl$_2$$\cdot$2CH$_3$CN: C, 77.31; H, 5.18; N, 6.77. Found: C, 77.13; H, 4.91; N, 6.50.
Synthesis of complex: \([\text{FeCu}_4(1)_2]^{6+}\)

To a solution of nanoswitch 1 (560 µg, 0.396 µmol) in CD$_2$Cl$_2$, a standard solution of Fe(BF$_4$)$_2$•6H$_2$O (66.8 µg, 0.198 µmol) in CD$_3$CN was added. Thereafter, [Cu(CH$_3$CN)$_4$]PF$_6$ (295 µg, 0.792 µmol) was added as a solid and $^1$H NMR was measured without further purification. Yield: Quantitative.

$\text{Mp:} > 250 ^\circ \text{C. IR (KBr):} \quad \tilde{\nu} = 513, 721, 809, 948, 1124, 1234, 1457, 1528, 1538, 1781, 2219, 2318, 2714, 2824, 2946 \text{ cm}^{-1}$.  

$^1$H-NMR (400 MHz, CD$_3$CN:CD$_2$Cl$_2$ 1:5, 298 K): $\delta =$ 1.85 (s, 24H, 13-H), 1.94 (s, 24H, 10-H), 2.32 (s, 12H, 11-H), 2.59 (s, 24H, 12-H), 6.97 (s, 8H, 9-H), 7.04 (dd, $^3J = 8.0$, $^3J = 4.8$ Hz, 4H, b-H), 7.13 (d, $^3J = 4.8$ Hz, 4H, a-H), 7.42–7.50 (m, 4H, i+j-H), 7.59 (d, $^3J = 8.2$ Hz, 4H, 3/8-H), 7.67–7.79 (m, 8H, h+k+c-H), 7.81 (d, $^3J = 8.2$ Hz, 4H, 8/3-H), 7.84 (s, 2H, n-H), 7.88 (s, 4H, m+1-H), 7.98 (d, $^3J = 8.4$ Hz, 4H, g/f-H), 8.09 (s, 8H, [5+6]-H), 8.34 (d, $^3J = 8.4$ Hz, 4H, `g'-H), 8.48 (d, $^3J = 8.0$ Hz, 4H, d-H), 8.53 (d, $^3J = 8.2$ Hz, 4H, 4/7-H), 8.60 (d, $^3J = 8.2$ Hz, 4H, 7/4-H), 9.06 (s, 4H, e-H) ppm. ESI-MS: m/z (%) = 1525.7 (25) [FeCu(1)$_2$(BF$_4$)]$^{2+}$, 1443.2 (100) [Fe(1)$_2$]$^{2+}$, 1415.0 (15) [1+H]$^+$, 1040.1 (35) [FeCu$_2$(1)$_2$(BF$_4$)(H$_2$O)]$^{3+}$, 962.3 (20) [Fe(1)$_2$(H)]$^{3+}$.  

Elemental analysis: Anal. Calcd for C$_{206}$H$_{158}$BCu$_4$F$_{28}$FeN$_{14}$P$_4$: C, 65.00; H, 4.18; N, 5.15. Found: C, 64.64; H, 4.34; N, 5.50.
Synthesis of complex: $[\text{Cu(2)}]^+$

To a solution of nanoswitch 2 (610 µg, 0.343 µmol) in CD$_2$Cl$_2$ (500 µL), [Cu(CH$_3$CN)$_4$]PF$_6$ (128 µg, 0.343 µmol) was added as a solid. Subsequently, the $^1$H NMR was measured without further purification. Yield: Quantitative (two diastereomers 50:50). **Mp:** > 250 ºC. **IR (KBr):** $\tilde{\nu} = 521, 573, 621, 823, 915, 983, 1054, 1075, 1161, 1278, 1398, 1478, 1583, 1627, 2218, 2317, 2776, 2814, 2977$ cm$^{-1}$. **$^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K):** $\delta = 0.24$ (s, 4.5H, TMS-H), 0.27 (s, 4.5H, TMS-H), 1.59 (s, 3H, 12-H), 1.72 (s, 3H, 12-H), 1.77 (s, 3H, 13-H), 1.90 (s, 3H, 10-H), 1.93 (s, 3H, 13-H), 1.94 (s, 3H, 10-H), 1.95 (s, 3H, 13u/12u-H), 2.00 (s, 1.5H, 11-H), 2.00 (s, 1.5H, 11-H), 2.04 (s, 3H, 10u-H), 2.05 (s, 3H, 10u-H), 2.33 (s, 1.5H, 11u-H), 2.47 (s, 3H, 12u/13u-H), 2.52 (s, 3H, 13u/12u-H), 2.55 (s, 3H, 12u/13u-H), 6.33 (s, 1H, 9-H), 6.33 (s, 1H, 9-H), 6.64 (ddd, $^3J = 4.8$ Hz, $^4J = 1.6$ Hz, $^5J = 0.8$ Hz, 1H, a-H), 6.74 (ddd, $^3J = 7.6$ Hz, $^3J = 4.8$ Hz, $^4J = 1.0$ Hz, 1H, b-H), 6.95 (s, 1H, 9u-H), 6.96 (s, 1H, 9u-H), 7.21–7.30 (m, 5H, c,tpc-H), 7.32–7.58 (m, 12H, tpc,n,o,l/k-H), 7.52–7.60 (m, 11H, d,3u,8u,m,p,k/Ltpc-H), 7.68 (d, $^3J = 8.2$ Hz, 1H, 8/3-H), 7.87 (s, 1H, j-H), 7.86–7.89 (m, 5H, 5,6,5u,6u,g-H), 7.95 (d, $^3J = 8.2$ Hz, 1H, 3/8-H), 8.00–8.07 (m, 2H, f,e-H), 8.08 (d, $^3J = 8.9$ Hz, 1H, i-H), 8.16 (d, $^3J = 8.9$ Hz, 1H, h-H), 8.33–8.38 (m, 2H, 4u,7u-H), 8.44 (d, $^3J = 8.2$ Hz, 1H, 7/4-H), 8.69 (d, $^3J = 8.2$ Hz, 1H, 4/7-H) ppm. **ESI-MS:** $m/z$ (%) = 1840.7 (100) $[\text{Cu(2)}]^+$. **Elemental analysis:** Anal. Calcd for C$_{129}$H$_{101}$CuF$_6$N$_7$PSi•3CH$_2$Cl$_2$•CH$_3$CN: C, 70.54; H, 4.86; N, 4.91. Found: C, 70.88; H, 4.95; N, 5.01.
Synthesis of complex $[\text{Cu}_2(2)]^{2+}$

Compound 2 (630 µg, 0.354 µmol) and [Cu(CH$_3$CN)$_4$]PF$_6$ (264 µg, 0.708 µmol) were placed in an NMR tube as solid and dissolved in CD$_2$Cl$_2$ (500 µL). Subsequently, $^1$H NMR was measured without further purification. Yield: Quantitative (four diastereomers 30:40:15:15).

$\text{Mp: } > 250 ^\circ \text{C. IR (KBr): } \nu \sim \nu = 517, 558, 632, 815, 947, 1015, 1049, 1159, 1247, 1349, 1419, 1592, 1626, 2219, 2321, 2746, 2852, 2973 \text{cm}^{-1}$.  

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, 298 K): $\delta = 0.22$ (s, 1.35H, TMS-H), 0.24 (s, 1.35H, TMS-H), 0.25 (s, 3.60H, TMS-H), 0.28 (s, 2.70H, TMS-H), 1.59–1.61 (m, 3H, 12-H), 1.73–1.75 (m, 3H, 12-H), 1.77 (s, 3H, 13-H), 1.90–1.91 (m, 3H, 10-H), 1.93–1.96 (m, 9H, 11,13c/12c-H), 2.01–2.03 (m, 3H, 10c-H), 2.04 (s, 3H, 10c-H), 2.05 (s, 3H, 10-H), 2.35–2.38 (m, 3H, 11c-H), 2.47–2.48 (m, 3H, 12c/13c-H), 2.55 (s, 3H, 13c/12c-H), 2.58 (s, 3H, 12c/13c-H), 6.27–6.30 (m, 1H, 9-H), 6.33–6.35 (m, 1H, 9-H), 6.51–6.66 (m, 1H, a-H), 6.72–6.78 (m, 1H, b-H), 7.02 (s, 1H, 9c-H), 7.04 (s, 1H, 9c-H), 7.22–7.49 (m, 17H, tpc,c,n,o,l/k-H), 7.52–7.61 (m, 9H, d,k/l,m,p,tpc-H), 7.67–7.70 (m, 8/3-H, 1H), 7.86–7.97 (m, 7H, 3/8,3c,4c,5,6,g,j/H), 7.99–8.10 (m, 3H, f,e,i-H), 8.16 (s, 2H, 5c,6c-H), 8.17 (d, $^3J = 8.9$ Hz, 1H, h-H), 8.43–8.46 (m, 1H, 7/4-H), 8.67–8.72 (m, 3H, 4/7, 4c/7c-H) ppm.  

ESI-MS: $m/z$ (%) = 1840.6 (10) [Cu(2)]$^+$, 951.8 (100) [Cu$_2$(2)]$^{2+}$.  

Elemental analysis: Anal. Calcd for C$_{129}$H$_{101}$Cu$_2$F$_{12}$N$_7$P$_2$Si•CH$_3$CN•2H$_2$O: C, 69.27; H, 4.79; N, 4.93.  

Found: C, 69.10; H, 4.71; N, 5.02.
Synthesis of complex: $[\text{Fe}(2)_2]^{2+}$

To a solution of nanoswitch 2 (643 µg, 0.362 µmol) in CD$_2$Cl$_2$ (420 µL), a standard solution Fe(BF$_4$)$_2$•6H$_2$O (61.1 µg, 0.181 µmol) in CD$_3$CN (80 µL) was added. Subsequently, the $^1$H NMR was measured without further purification. Yield: Quantitative. Mp: > 250 ºC. IR (KBr): $\tilde{\nu}$ = 613, 814, 953, 1032, 1078, 1261, 1263, 1371, 1594, 1781, 2218, 2317, 2781, 2824, 2971 cm$^{-1}$. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN, 5:1, 298 K): $\delta$ = 0.21 (s, 18H, TMS-H), 1.99 (s, 24H, 13-H), 2.03 (s, 24H, 10-H), 2.33 (s, 12H, 11-H), 2.54 (s, 24H, 12-H), 6.95 (s, 8H, 9-H), 6.99 (d, $^3J = 1.8$ Hz, 2H, j-H), 7.04–7.10 (m, 10H, a,tpc-H), 7.12–7.19 (m, 14H, b,tpc-H), 7.35–7.43 (m, 16H, tpc,n,o-H), 7.45 (d, $^3J = 8.3$ Hz, 4H, l/k-H), 7.50 (d, $^3J = 8.3$ Hz, 4H, k/l-H), 7.54–7.61 (m, 12H, 3,8,m,p-H), 7.90 (td, $^3J = 7.4$ Hz, $^4J = 1.2$ Hz, 2H, c-H), 7.97–7.93 (m, 8H, 5,6-H), 7.99 (dd, $^3J = 8.2$ Hz, $^4J = 1.8$ Hz, 2H, i-H), 8.36–8.42 (m, 8H, 4,7-H), 8.47 (d, $^3J = 7.4$ Hz, 2H, d-H), 8.53 (d, $^3J = 8.2$ Hz, 2H, h-H), 8.78 (t, $^3J = 8.2$ Hz, 2H, f-H), 8.93 (d, $^3J = 8.2$ Hz, 2H, e/g-H), 9.00 (d, $^3J = 8.2$ Hz, 2H, g/e-H) ppm. ESI-MS: $m/z$ (%) = 1804.4 (100) $[\text{Fe}(2)_2]^{2+}$. Elemental analysis: Anal. Calcd for C$_{258}$H$_{202}$BF$_4$FeN$_{14}$Si$_2$• 2CH$_3$CN•2CH$_2$Cl$_2$: C, 80.29; H, 5.41; N, 5.67. Found: C, 79.85; H, 5.47; N, 5.29.
Synthesis of complex [FeCu₄(2)₂]⁶⁺

To a solution of nanoswitch 2 (661 µg, 0.372 µmol) in CD₂Cl₂ (420 µL), a standard solution in CD₃CN (80 µL) of Fe(BF₄)₂•6H₂O (62.8 µg, 0.186 µmol) was added. [Cu(CH₃CN)₄]PF₆ (277 µg, 0.744 µmol) was then added as a solid. Subsequently, the ¹H NMR was measured without further purification. Yield: Quantitative. Mp: > 250 ºC. IR (KBr): ν ~ν ~ = 526, 632, 842, 913, 1043, 1061, 1284, 1379, 1593, 1778, 2221, 2322, 2717, 2983 cm⁻¹. ¹H NMR (400 MHz, CD₂Cl₂:CD₃CN, 298 K): δ = 0.20 (s, 18H, TMS-H), 1.94 (s, 24H, 13c-H), 2.03 (s, 24H, 10c-H), 2.32 (s, 12H, 11c-H), 2.54 (s, 24H, 12c-H), 6.98–7.03 (m, 10H, j,9c-H), 7.04–7.08 (m, 10H, a,tpc-H), 7.11–7.17 (m, 14H, b,tpc-H), 7.32–7.42 (m, 16H, tpc,n,o-H), 7.45 (d, 3J = 8.2 Hz, 4H, l/k-H), 7.50 (d, 3J = 8.2 Hz, 4H, k/l-H), 7.54–7.61 (m, 4H, m,p-H), 7.81 (m, 8H, 3c,8c-H), 7.89 (td, 3J = 7.4 Hz, 4J = 1.2 Hz, 2H, c-H), 7.99 (dd, 3J = 8.2 Hz, 4J = 1.8 Hz, 2H, i-H), 8.10 (s, 8H, 5c,6c-H), 8.45 (d, 3J = 7.4 Hz, 2H, d-H), 8.50 (d, 3J = 8.2 Hz, 2H, h-H), 8.60–8.63 (m, 8H, 4c,7c-H), 8.76 (t, 3J = 8.2 Hz, 2H, f-H), 8.90 (d, 3J = 8.2 Hz, 2H, e/g-H), 8.97 (d, 3J = 8.2 Hz, 2H, g/e-H) ppm. ESI-MS: m/z (%) = 1395.5 (100) [FeCu₄(2)₂+2BF₄⁺+PF₆]⁺, 801.6 (12) [FeCu₄(2)₂+PF₆]⁺. Elemental analysis: Anal. Calcd for C₂₅₈H₂₃₀BCu₄F₂₈FeN₁₄P₄Si₂•2CH₃CN•CH₂Cl₂: C, 67.23; H, 4.51; N, 4.77%; Found: C, 67.19; H, 4.59; N, 5.08.
3. NMR spectra

**Figure S1.** $^{1}H$ NMR spectrum of 7 in CDCl$_3$ (400 MHz, 298 K).

**Figure S2.** $^{1}H$-$^{1}H$ COSY spectrum of 7 in CDCl$_3$ (400 MHz, 298 K).
**Figure S3.** $^{13}$C NMR spectrum of 7 in CDCl$_3$ (100 MHz, 298 K).

**Figure S4.** $^1$H NMR spectrum of 1 in CD$_2$Cl$_2$ (400 MHz, 298 K).
Figure S5. $^1$H-$^1$H COSY spectrum of 1 in CD$_2$Cl$_2$ (400 MHz, 298 K).

Figure S6. $^{13}$C NMR spectrum of 1 in CD$_2$Cl$_2$ (100 MHz, 298 K).
Figure S7. $^1$H NMR spectrum of 3 in CD$_2$Cl$_2$ (400 MHz, 298 K).

Figure S8. $^1$H-$^1$H COSY spectrum of 3 in CD$_2$Cl$_2$ (400 MHz, 298 K).
Figure S9. $^{13}$C NMR spectrum of 3 in CD$_2$Cl$_2$ (100 MHz, 298 K).

Figure S10. $^1$H NMR spectrum of 12 in CD$_2$Cl$_2$ (400 MHz, 298 K).
Figure S11. $^1$H-$^1$H COSY spectrum of 12 in CD$_2$Cl$_2$ (400 MHz, 298 K).

Figure S12. $^{13}$C NMR spectrum of 12 in CD$_2$Cl$_2$ (100 MHz, 298 K).
**Figure S13.** $^1$H NMR spectrum of 13 in CDCl$_3$ (400 MHz, 298 K).

**Figure S14.** $^1$H-$^1$H COSY spectrum of 13 in CDCl$_3$ (400 MHz, 298 K).
Figure S15. $^{13}$C NMR spectrum of 13 in CDCl$_3$ (100 MHz, 298 K).

Figure S16. $^1$H NMR spectrum of 15 in CDCl$_3$ (400 MHz, 298 K).
Figure S17. $^1$H-$^1$H COSY spectrum of 15 in CDCl$_3$ (400 MHz, 298 K).

Figure S18. $^{13}$C NMR spectrum of 15 in CDCl$_3$ (100 MHz, 298 K).
Figure S19. $^1$H NMR spectrum of $2$ in CD$_2$Cl$_2$ (400 MHz, 298 K).
Figure S20. $^1$H-$^1$H COSY spectrum of 2 in CD$_2$Cl$_2$ (400 MHz, 298 K).

Figure S21. $^{13}$C NMR spectrum of 2 in CD$_2$Cl$_2$ (100 MHz, 298 K).
Figure S22. $^1$H NMR spectrum of [Cu(I)]$^+$ in CD$_2$Cl$_2$ (500 MHz, 298 K).

Figure S23. $^1$H-$^1$H COSY spectrum of of [Cu(I)]$^+$ in CD$_2$Cl$_2$ (500 MHz, 298 K).
Figure S24. $^1$H NMR spectrum of [Cu$_2$(I)$_2$]$^{2+}$ in CD$_2$Cl$_2$ (500 MHz, 298 K).

Figure S25. $^1$H-$^1$H COSY spectrum of [Cu$_2$(I)$_2$]$^{2+}$ in CD$_2$Cl$_2$ (500 MHz, 298 K).
Figure S26. $^1$H NMR spectrum of [FeCu$_4$(I)$_2$]$^{6+}$ in CD$_2$Cl$_2$:CD$_3$CN (5:1) (400 MHz, 298 K).

Figure S27. $^1$H-$^1$H COSY spectrum of [FeCu$_4$(I)$_2$]$^{6+}$ in CD$_2$Cl$_2$:CD$_3$CN (5:1) (400 MHz, 298 K).
Figure S28. $^1$H NMR spectrum of $[\text{Fe (1)}_2]^{2+}$ in CD$_2$Cl$_2$:CD$_3$CN (5:1) (400 MHz, 298 K).

Figure S29. $^1$H-$^1$H COSY spectrum of $[\text{Fe (1)}_2]^{2+}$ in CD$_2$Cl$_2$:CD$_3$CN (5:1) (400 MHz, 298 K).
Figure S30. $^1$H NMR spectrum of State I$_2 = [\text{Cu(2)}]^+$ (CD$_2$Cl$_2$, 400 MHz, 298 K).

Figure S31. $^1$H-$^1$H COSY spectrum of State I$_2 = [\text{Cu(2)}]^+$ in (CD$_2$Cl$_2$, 400 MHz, 298 K).
Figure S32. $^1$H NMR spectrum of State II$_2 = [\text{Cu}_2(2)]^{2+}$ (CD$_2$Cl$_2$, 400 MHz, 298 K).

Figure S33. $^1$H-$^1$H COSY spectrum of State II$_2 = [\text{Cu}_2(2)]^{2+}$ in (CD$_2$Cl$_2$, 400 MHz, 298 K).
Figure S34. $^1$H NMR spectrum of State IV$_2 = [\text{Fe(2)}_2]^{2+}$ (400 MHz, CD$_2$Cl$_2$:CD$_3$CN (5:1), 298 K).

Figure S35. $^1$H-$^1$H COSY spectrum of State IV$_2 = [\text{Fe(2)}_2]^{2+}$ in (400 MHz, CD$_2$Cl$_2$:CD$_3$CN (5:1), 298 K).
Figure S36. $^1$H NMR spectrum of State III$_2$ = [Cu$_4$Fe$_2$(2)$_2$]$^{6+}$ (400 MHz, CD$_2$Cl$_2$:CD$_3$CN (5:1), 298 K).

Figure S37. $^1$H-$^1$H COSY spectrum of State III$_2$ = [Cu$_4$Fe$_2$(2)$_2$]$^{6+}$ in (400 MHz, CD$_2$Cl$_2$:CD$_3$CN (5:1), 298 K).
Figure S38. Partial $^1$H NMR (400 MHz, 298K) of (a) [Cu(1)]$^+$ (in CD$_2$Cl$_2$), (b) [Cu$_2$(1)]$^{2+}$ (in CD$_2$Cl$_2$), (c) [FeCu$_4$(1)$_2$]$^{6+}$ (in CD$_2$Cl$_2$:CD$_3$CN = 5:1), (d) [Fe(1)$_2$]$^{2+}$ (in CD$_2$Cl$_2$:CD$_3$CN = 5:1).
Switching cycle

Ligand 1 (or 2) (0.46 µmol) was dissolved in 450 µL of CD₂Cl₂. Addition of 1.0 equiv. of [Cu(CH₃CN)₄]PF₆ (0.46 µmol) to the above solution produced state I, i.e., [Cu(1)]⁺ quantitatively (¹H NMR). After addition of one further equivalent of [Cu(CH₃CN)₄]PF₆ (0.46 µmol), the ¹H NMR confirmed the formation of [Cu₂(1)]²⁺ (state II). Thereafter, 0.5 equiv. of FeBF₄•6H₂O (0.23 µmol) was added as a standard solution in CD₃CN. The single set of phenanthroline signals in the ¹H NMR confirmed the formation of [FeCu₁(1)]⁶⁺ (state III). Then, removal copper(I) ions by addition of 2.0 equiv. of cyclam (0.92 µmol) yielded state IV, [Fe(1)₂]²⁺. Finally, iron(II) ions were removed by addition of 0.5 equiv. (0.23 µmol) of hexacyclen in that way regenerating ligand 1 (or 2). The reversibility of the switching cycle was demonstrated up to two cycles (states I→II→III→IV→I).

Figure S39. Partial ¹H NMR (400 MHz, 298K) of (a) [Cu(1)]⁺ in CD₂Cl₂, (b) after addition of 1.0 equiv. of [Cu(CH₃CN)₄]PF₆ (with respect to 1) to the solution of a; ¹H NMR confirmed the formation of [Cu₂(1)]²⁺, (c) after addition of 0.5 equiv. of FeBF₄•6H₂O as a standard solution in CD₃CN (with respect to 1) to the solution of b; ¹H NMR confirmed the formation of
[FeCu(1)2]+, (d) after addition of 2.0 equiv. of cyclam (with respect to 1) to the solution of c; 1H NMR confirmed the formation of [Fe(1)2]2+, (e) after addition of 0.5 equiv. of hexacyclen followed by addition of 1.0 equiv. [Cu(CH3CN)4]PF6 to the solution d, (f) after addition of 1.0 equiv. of [Cu(CH3CN)4]PF6 (with respect to 1) to the solution of e, (g) after addition of 0.5 equiv. of FeBF4·6H2O as a standard solution in CD3CN (with respect to 1) to f, (h) after addition of 2.0 equiv. of cyclam (with respect to 1) to the solution of g; (i) after addition of 0.5 equiv. of hexacyclen to solution h.
Figure S40. Partial $^1$H NMR (400 MHz, 298K) of (a) [Cu($^2$)]$^+$ in CD$_2$Cl$_2$, (b) after addition of 1.0 equiv. of [Cu(CH$_3$CN)$_4$]PF$_6$ (with respect to 2) to the solution of a; $^1$H NMR confirmed the formation of [Cu$_2$(2)]$^{2+}$, (c) after addition of 0.5 equiv. of FeBF$_4$·6H$_2$O as a standard solution in CD$_3$CN (with respect to 2) to the solution of b; $^1$H NMR confirmed the formation of [FeCu$_4$(2)$_2$]$_6^{6+}$, (d) after addition of 2.0 equiv. of cyclam (with respect to 2) to the solution of c; $^1$H NMR confirmed the formation of [Fe(2)$_2$]$^{2+}$, (e) after addition of 0.5 equiv. of hexacyclen followed by addition of 1.0 equiv. [Cu(CH$_3$CN)$_4$]PF$_6$ to the solution d, (f) after addition of 1.0 equiv. of [Cu(CH$_3$CN)$_4$]PF$_6$ (with respect to 2) to the solution of e, (g) after addition of 0.5 equiv. of FeBF$_4$·6H$_2$O as a standard solution in CD$_3$CN (with respect to 2) to f, (h) after addition of 2.0 equiv. of cyclam (with respect to 2) to the solution of g; (i) after addition of 0.5 equiv. of hexacyclen to solution h.
Figure S41. Partial $^1$H NMR (CD$_2$Cl$_2$, 400 MHz, 298 K) of [Cu$_2$(3)]$^{2+}$ in presence of (a) each 1.0 equiv. of pyridin-4-yl-methanol (A1) and 1-acetylimidazole (B), (b) 2.0 equiv. of B, and (c) 2.0 equiv. of A1.
Rate constant calculation by volume intensity of the ROESY crosses peaks

Speed calculation:

\[ \frac{I_D}{I_C} = \frac{1 - kt_M}{kt_M} \quad \text{or} \quad k = \frac{1}{[t_M(I_D/I_C + 1)]} \]

Where \( I_D \): intensity of diagonal peak

\( I_C \): intensity of cross peak

\( t_M \): mixing time (0.3 s)

Eyring Equation; \( k = \left( k_B T/h \right) \exp \left( -\frac{\Delta G^\ddagger}{RT} \right) \)

\( k_B \): Boltzmann constant

\( h \): Planck’s constant

**Figure S42.** Partial \(^1\text{H}-^1\text{H}\) ROESY (400 MHz, CD\(_2\)Cl\(_2\): CD\(_3\)CN (5:1)) of [Cu\(_2(\text{I})\)]\(^{2+}\) with volume intensity of cross and diagonal peaks. The rotational frequency is determined to be \( k = 1.34 \text{ Hz} \). Free energy of activation \( \Delta G^\ddagger \_{298} = 72.6 \text{ kJ mol}^{-1} \).
5. Catalytic experiments

General procedure: The solid substrates (A1/A2, B) were placed in an NMR tube and the separately prepared catalyst (see chapter 2) in CD₂Cl₂:CD₃CN (5:1, 500 µL) was added. The mixture was heated at 50 °C for 2 h and ¹H NMR was measured without further purification. The yields of individual reactions were calculated using 1,3,5-trimethoxybenzene (16) as an internal standard (singlet at δ = 6.04 ppm).

![Diagram of chemical reactions](image)

**Figure S43.** ¹H NMR (400 MHz, CD₂Cl₂:CD₃CN = 5:1, 298 K) spectrum obtained after heating the reaction mixture of compounds A1, B (≈ 30.0 mM) and standard 1,3,5-trimethoxybenzene (16) in 1:1:1 ratio at 50 °C for 2 h. No formation of product C1 was observed in ¹H NMR.
Figure S44. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained after heating the reaction mixture of compounds 3 ($\approx$ 3.0 mM), [Cu(CH$_3$CN)$_4$]PF$_6$ A1, B and standard 16 in 1:2:10:10:10 ratio at 50 °C for 2 h. 33% of product C1 was observed in $^1$H NMR.

Figure S45. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained after heating the reaction mixture of compounds 4 ($\approx$ 6.0 mM), [Cu(CH$_3$CN)$_4$]PF$_6$ A1, B and standard 16 in 1:1:5:5:5 ratio at 50 °C for 2 h. Only 2% of product C1 was observed in $^1$H NMR.
Figure S46. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained after heating the reaction mixture of compounds 17 ($\approx$ 3.0 mM), FeBF$_4$•6H$_2$O, A1, B and standard 16 in 2:1:20:20:20 ratio at 50 °C for 2 h. No formation of product C1 was observed in $^1$H NMR.

Figure S47. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained after heating the reaction mixture of compounds 1 ($\approx$ 3.0 mM), [Cu(CH$_3$CN)$_4$]PF$_6$, A1, B and standard 16 in 1:2:10:10:10 ratio at 50 °C for 2 h. No formation of product C1 was detected in $^1$H NMR.
Figure S48. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained after heating the reaction mixture of compounds 1 ($\approx$ 3.0 mM), [Cu(CH$_3$CN)$_4$]PF$_6$, FeBF$_4$$\cdot$6H$_2$O, A1, B and standard 16 in 1:2:0.5:10:10:10 ratio at 50 °C for 2 h. 33% of product C1 formation was observed in $^1$H NMR.

Figure S49. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained after heating the reaction mixture of compounds 2 ($\approx$ 3.0 mM), [Cu(CH$_3$CN)$_4$]PF$_6$, A2, B and standard 16 in 1:2:10:10:10 ratio at 50 °C for 2 h. No formation of product C2 was observed in $^1$H NMR.
Figure S50. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained after heating the reaction mixture of compounds 2 ($\approx$ 3.0 mM), [Cu(CH$_3$CN)$_4$]PF$_6$, FeBF$_4$•6H$_2$O, A2, B and standard 16 in 1:2:0.5:10:10:10 ratio at 50 °C for 2 h. 26% of product C2 was observed in $^1$H NMR.

Figure S51. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained after heating the reaction mixture of compounds 2 ($\approx$ 3.0 mM), [Cu(CH$_3$CN)$_4$]PF$_6$, FeBF$_4$•6H$_2$O, A1, B and standard 16 in 1:2:0.5:10:10:10 ratio at 50 °C for 2 h. Only 2% of product C1 was observed in $^1$H NMR.
Figure S52. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained after heating the reaction mixture of compounds 3 ($\approx$ 3.0 mM), [Cu(CH$_3$CN)$_4$]PF$_6$ A2, B and standard 16 in 1:2:10:10:10 ratio at 50 °C for 2 h. No formation of product C2 was observed in $^1$H NMR.
Figure S53. $^1$H NMR (500 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained (A) after heating the reaction mixture of compounds 1 ($\approx 3.0$ mM), $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ A1, B and standard 16 in 1:2:10:10:10 ratio at 50 °C for 2 h; no product C1 formation was observed in $^1$H NMR. (B) After addition of 0.5 equiv. of FeBF$_4$$\cdot$6H$_2$O and heating the mixture for another 2 h, 33% of product C1 formed. (C) After addition of 0.5 equiv. of hexacyclen and consumed amount of substrates A1 and B, the mixture was heated for another 2 h. Only 1% of the product C1 was formed. (D) After addition of 0.5 equiv. of FeBF$_4$$\cdot$6H$_2$O and heating the mixture for another 2 h, 26% of extra product C1 formed. (E) After addition of 0.5 equiv. of hexacyclen followed by consumed amount of A1 and B and heating the mixture for another 2 h. Only 1% of the product C1 was formed.
Figure S54. $^1$H NMR (500 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained (A) after heating the reaction mixture of compounds 2 (≈ 3.0 mM), [Cu(CH$_3$CN)$_4$]PF$_6$ A2, B and standard 16 in 1:2:10:10:10 ratio at 50 °C for 2 h; no product C2 formation was observed in $^1$H NMR. (B) After addition of 0.5 equiv. of FeBF$_4$•6H$_2$O and heating the mixture for another 2 h, 26% of product C2 formed. (C) After addition of 0.5 equiv. of hexacyclen followed by consumed amount of A1 and B and heating the mixture for another 2 h. No product C2 was formed. (D) After addition of 0.5 equiv. of FeBF$_4$•6H$_2$O and heating the mixture for another 2 h, 20% of extra product C2 formed. (E) After addition of 0.5 equiv. of hexacyclen followed by consumed amount of A1 and B and heating the mixture for another 2 h. No extra product C2 was formed.
**Figure S55.** Partial $^1$H NMR of mixture of (a) nanoswitch 2, (b) [Cu(1)]$^{2+}$, (c) After addition of 1.0 equiv. of [Cu(CH$_3$CN)$_4$]PF$_6$ to a 1:1 mixture of 1 and 2; complex [Cu(1)]$^{2+}$ formed quantitatively whereas 2 remained unaffected.

**Figure S56.** Partial $^1$H NMR of mixture of (A) [Cu$_2$(1)]$^{2+}$ and [Cu$_2$(2)]$^{2+}$ in CD$_2$Cl$_2$, (B) after addition of 0.5 equiv. of iron(II) for selective formation of [Cu$_2$(1)]$^{2+}$ and [FeCu$_4$(2)]$^{6+}$, (C) after addition of 0.5 equiv. of hexacyclen to the solution B, (D) after addition of 0.5 equiv. of iron(II) (E) after addition of 0.5 equiv. of hexacyclen.
Figure S57. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained after heating the reaction mixture of compounds 4 ($\approx$ 6.0 mM), [Cu(CH$_3$CN)$_4$]PF$_6$, A1, A2, B and standard 16 in 2:2:10:10:10:10 ratio at 50 °C for 24 h. 14% of C1 and 11% of C2 formation was observed in $^1$H NMR.

Figure S58. $^1$H NMR (500 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained after heating the reaction mixture of switch 1 ($\approx$ 3.0 mM), 2, [Cu(CH$_3$CN)$_4$]PF$_6$, FeBF$_4$•6H$_2$O, A1, A2, B and standard 16 in 1:1:4:0.5:10:10:10:10 ratio at 50 °C for 2 h. 3% of C1 and 17% of C2 formation was observed in $^1$H NMR.
6. ESI-MS Spectra

Figure S59. ESI-MS of compound 3 after protonation.

Figure S60. ESI-MS of compound 7 after protonation.
Figure S61. ESI-MS of nanoswitch 1 after protonation.

Figure S62. ESI-MS of compound 12 after protonation.
Figure S63. ESI-MS of compound 13 after protonation.

Figure S64. ESI-MS of compound 15 after protonation.
**Figure S65.** ESI-MS of nanoswitch 2 after protonation.

**Figure S66.** ESI-MS of [Cu(I)]\(^+\) (State I).
Figure S67. ESI-MS of [Cu$_2$(1)]$^{2+}$ (State II$_1$).

Figure S68. ESI-MS of [FeCu$_4$(1)$_2$]$^{6+}$ (State III$_1$).
Figure S69. ESI-MS of [Fe(1)]^{2+} (State IV).

Figure S70. ESI-MS of complex [Cu(2)]^{+} (State I).
**Figure S71.** ESI-MS of complex $[\text{Cu}_2(\text{2})]^2+$ (State II$_2$).

**Figure S72.** ESI-MS of complex $[\text{Fe}(\text{2})_2]^2+$ (State IV$_2$).
**Figure S73.** ESI-MS of complex $[\text{FeCu}_4(2)_2]^{6+}$ (State III$_2$).

7. UV-vis Spectra

**Figure S74.** Comparison of UV-vis spectra ($1.25 \times 10^{-4}$ M in CH$_2$Cl$_2$) of $[\text{Cu}_2(1)]^{2+}$ = State II$_1$ and $[\text{FeCu}_4(1)_2]^{6+}$ = State III$_1$ at 298 K.
8. Computational Studies

DFT-equilibrium geometry optimization of copper(I) loaded bis-phenanthroline cavity part with corresponding substrates (A1/A2 and B) of triangular switch (1) and tetrahedral switch (2) were calculated using SPARTAN '18 MECHANICS (Method: B3LYP; Basis Set: 6-31G**).

The distance between two Cu\(^{+}\) atoms of PhenAr\(_2\) stations in triangular switch (1) and tetrahedral switch (2) are 14.9 Å, and 18.0 Å, respectively.

Figure S75. DFT optimized structure of [Cu(3)(A1)(B)]\(^{2+}\).
Figure S76. DFT optimized structure of the cavity part of [Cu2(A2)(B)].
| Protein  | ID   | Start | End   | Value  |
|----------|------|-------|-------|--------|
| HETA TM  | 82 C | 5.254 | 5.666 | -4.523 |
| HETA TM  | 83 C | 6.156 | 4.061 | -2.797 |
| HETA TM  | 84 C | 4.330 | 6.655 | -4.919 |
| HETA TM  | 85 C | 2.368 | 8.223 | -4.434 |
| HETA TM  | 86 H | 2.310 | 8.292 | -1.711 |
| HETA TM  | 87 H | 2.499 | 6.838 | -0.717 |
| HETA TM  | 88 H | 1.277 | 6.893 | -1.991 |
| HETA TM  | 89 C | 6.345 | 5.175 | -5.453 |
| HETA TM  | 90 H | 5.883 | 3.642 | -1.828 |
| HETA TM  | 91 H | 7.176 | 4.461 | -2.710 |
| HETA TM  | 92 H | 6.199 | 3.245 | -3.527 |
| HETA TM  | 93 C | 4.391 | 7.217 | -6.301 |
| HETA TM  | 94 H | 1.361 | 7.984 | -4.075 |
| HETA TM  | 95 H | 2.307 | 8.343 | -5.517 |
| HETA TM  | 96 H | 2.624 | 9.203 | -4.009 |
| HETA TM  | 97 H | 6.402 | 7.572 | -6.377 |
| HETA TM  | 98 H | 1.579 | 4.122 | -5.730 |
| HETA TM  | 99 H | 7.325 | 5.232 | -4.968 |
| HETA TM  | 100 C| 4.853 | 8.539 | -6.510 |
| HETA TM  | 101 N| 3.995 | 6.449 | -7.324 |
| HETA TM  | 102 C| 4.891 | 9.067 | -7.781 |
| HETA TM  | 103 H| 5.173 | 9.121 | -5.653 |
| HETA TM  | 104 C| 4.038 | 6.962 | -8.588 |
| HETA TM  | 105 Cu| 3.284 | 4.557 | -7.377 |
| HETA TM  | 106 C| 4.472 | 8.277 | -8.875 |
| HETA TM  | 107 H| 5.243 | 10.081| -7.952 |
| HETA TM  | 108 C| 3.626 | 6.100 | -9.670 |
| HETA TM  | 109 N| 3.239 | 4.831 | -9.350 |
| HETA TM  | 110 C| 4.480 | 8.744 | -10.230|
| HETA TM  | 111 C| 3.657 | 6.588 | -10.997|
| HETA TM  | 112 C| 2.881 | 3.994 | -10.333|
| HETA TM  | 113 C| 4.086 | 7.932 | -11.251|
| HETA TM  | 114 H| 4.811 | 9.759 | -10.427|
| HETA TM  | 115 C| 3.270 | 5.692 | -12.018|
| HETA TM  | 116 C| 2.892 | 4.410 | -11.687|
| HETA TM  | 117 C| 2.503 | 2.587 | -10.005|
| HETA TM  | 118 H| 4.097 | 8.288 | -12.277|
| HETA TM  | 119 H| 3.287 | 6.016 | -13.055|
| HETA TM  | 120 H| 2.616 | 3.698 | -12.456|
| HETA TM  | 121 C| 3.474 | 1.701 | -9.482 |
| HETA TM  | 122 C| 1.207 | 2.114 | -10.312|
| HETA TM  | 123 C| 3.144 | 0.351 | -9.323 |
| HETA TM  | 124 C| 0.918 | 0.760 | -10.112|
| HETA TM  | 125 C| 1.877 | 0.146 | -9.630 |
| HETA TM  | 126 H| 3.907 | 0.333 | -8.954 |
| HETA TM  | 127 H| -0.082| 0.401 | -10.342|
| HETA TM  | 128 C| 3.091 | 3.816 | 6.301 |
| HETA TM  | 129 C| 3.789 | 4.455 | 7.333 |
| HETA TM  | 130 C| 1.878 | 4.391 | 5.879 |
| HETA TM  | 131 C| 3.281 | 5.609 | 7.939 |
| HETA TM  | 132 H| 4.742 | 4.065 | 7.672 |
| HETA TM  | 133 C| 1.366 | 5.534 | 6.486 |
| HETA TM  | 134 H| 1.334 | 3.942 | 5.053 |
| HETA TM  | 135 C| 2.067 | 6.150 | 7.526 |
| HETA TM  | 136 H| 3.847 | 6.083 | 8.736 |
| HETA TM  | 137 H| 0.424 | 5.951 | 6.139 |
| HETA TM  | 138 H| 1.673 | 7.045 | 8.000 |
| HETA TM  | 139 C| 4.983 | 2.059 | 6.104 |
| HETATM 198 H UNK 0001 | 2.315 -4.433 4.803 | CONECT 44 17 21 61 |
|--------------------------|--------------------------|--------------------------|
| HETATM 199 H UNK 0001 | 1.420 -3.044 2.588 | CONECT 45 12 46 47 48 |
| HETATM 200 N UNK 0001 | 1.840 -4.944 1.625 | CONECT 46 45 |
| HETATM 201 C UNK 0001 | 1.461 -4.631 0.292 | CONECT 47 45 |
| HETATM 202 C UNK 0001 | 1.616 -5.728 -0.728 | CONECT 48 45 |
| HETATM 203 H UNK 0001 | 1.078 -6.633 -0.428 | CONECT 49 14 50 51 52 |
| HETATM 204 H UNK 0001 | 1.226 -5.366 -1.679 | CONECT 50 49 |
| HETATM 205 H UNK 0001 | 2.673 -5.992 -0.851 | CONECT 51 49 |
| HETATM 206 O UNK 0001 | 1.041 -3.522 0.031 | CONECT 52 49 |
| HETATM 207 C UNK 0001 | -0.725 -0.989 1.734 | CONECT 53 13 54 55 56 |
| HETATM 208 H UNK 0001 | -1.183 -1.987 1.816 | CONECT 54 53 |
| HETATM 209 H UNK 0001 | -0.924 -0.458 2.669 | CONECT 55 53 |
| HETATM 210 N UNK 0001 | -4.573 3.164 -4.830 | CONECT 56 53 |
| HETATM 211 O UNK 0001 | 0.697 -1.105 1.648 | CONECT 57 15 58 59 60 |
| HETATM 212 H UNK 0001 | 0.899 -1.698 0.903 | CONECT 58 57 |

CONECT 1 2 6 7
CONECT 2 1 3 63
CONECT 3 2 4 64
CONECT 4 3 5 62
CONECT 5 4 6 8
CONECT 6 1 5 9
CONECT 7 1
CONECT 8 5
CONECT 9 6 10
CONECT 10 9 11
CONECT 11 10 12 13
CONECT 12 11 14 45
CONECT 13 11 15 53
CONECT 14 12 16 49
CONECT 15 13 16 57
CONECT 16 14 15 17
CONECT 17 16 18 44
CONECT 18 17 19 20
CONECT 19 18 22 23
CONECT 20 18
CONECT 21 22 24 44
CONECT 22 19 21 25
CONECT 23 19
CONECT 24 21 26 43
CONECT 25 22 27 28
CONECT 26 24 27 29
CONECT 27 25 26 31
CONECT 28 25
CONECT 29 26 32 33
CONECT 30 33 35 43
CONECT 31 27
CONECT 32 29
CONECT 33 29 30 34
CONECT 34 33
CONECT 35 30 36 37
CONECT 36 35 38 154
CONECT 37 35 39 150
CONECT 38 36 40 41
CONECT 39 37 40 42
CONECT 40 38 39 158
CONECT 41 38
CONECT 42 39
CONECT 43 24 30 61

S68
CONECT 102 100 106 107
CONECT 103 100
CONECT 104 101 106 108
CONECT 105 101 109 193
CONECT 106 102 104 110
CONECT 107 102
CONECT 108 104 111 109
CONECT 109 105 108 112
CONECT 110 106 113 114
CONECT 111 108 113 115
CONECT 112 109 116 117
CONECT 113 110 111 118
CONECT 114 110
CONECT 115 111 119 116
CONECT 116 112 115 120
CONECT 117 112 121 122
CONECT 118 113
CONECT 119 115
CONECT 120 116
CONECT 121 117 123 166
CONECT 122 117 124 170
CONECT 123 121 125 126
CONECT 124 122 125 127
CONECT 125 123 124 162
CONECT 126 123
CONECT 127 124
CONECT 128 64 129 130
CONECT 129 128 131 132
CONECT 130 128 133 134
CONECT 131 129 135 136
CONECT 132 129
CONECT 133 130 135 137
CONECT 134 130
CONECT 135 131 133 138
CONECT 136 131
CONECT 137 133
CONECT 138 135
CONECT 139 64 140 141
CONECT 140 139 142 143
CONECT 141 139 144 145
CONECT 142 140 146 147
CONECT 143 140
CONECT 144 141 146 148
CONECT 145 141
CONECT 146 142 144 149
CONECT 147 142
CONECT 148 144
CONECT 149 146
CONECT 150 37 151 152 153
CONECT 151 150
CONECT 152 150
CONECT 153 150
CONECT 154 36 155 156 157
CONECT 155 154
CONECT 156 154
CONECT 157 154

CONECT 158 40 159 160 161
CONECT 159 158
CONECT 160 158
CONECT 161 158
CONECT 162 125 163 164 165
CONECT 163 162
CONECT 164 162
CONECT 165 162
CONECT 166 121 167 168 169
CONECT 167 166
CONECT 168 166
CONECT 169 166
CONECT 170 122 171 172 173
CONECT 171 170
CONECT 172 170
CONECT 173 170
CONECT 174 176 177 210
CONECT 175 178 179 210
CONECT 176 174 180 181
CONECT 177 174
CONECT 178 175 180 182
CONECT 179 175
CONECT 180 176 178 183
CONECT 181 176
CONECT 182 178
CONECT 183 180 184 185
CONECT 184 183 186 187
CONECT 185 183 188 189
CONECT 186 184 190 191
CONECT 187 184
CONECT 188 185 190 192
CONECT 189 185
CONECT 190 186 188 207
CONECT 191 186
CONECT 192 188
CONECT 193 105 194 195
CONECT 194 193 196 200
CONECT 195 193 197 198
CONECT 196 194
CONECT 197 195 199 200
CONECT 198 195
CONECT 199 197
CONECT 200 194 197 201
CONECT 201 200 202 206
CONECT 202 201 203 204 205
CONECT 203 202
CONECT 204 202
CONECT 205 202
CONECT 206 201
CONECT 207 190 208 209 211
CONECT 208 207
CONECT 209 207
CONECT 210 61 174 175
CONECT 211 212 207
CONECT 212 211
END
9. References

1. P. K. Biswas, S. Saha, S. Gaikwad, Michael Schmittel, *J. Am. Chem. Soc.* **2020**, *142*, 7889–7897.

2. S. K. Samanta, M. Schmittel, *J. Am. Chem. Soc.* **2013**, *135*, 18794–18797.

3. S. Gaikwad, M. Schmittel, *J. Org. Chem.* **2017**, *82*, 343-352.

4. Y. Shao et al., Spartan 18, Wavefunction Inc. Irvine CA. *Mol.Phys.* **2015**, *113*, 184-215. DOI: 10.1080/00268976.2014.952696.