Electronic Supporting Information (SI)

Catalytically Active Nanorotor Reversibly Self-Assembled by Chemical Signaling within an Eight-Component Network

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1. Synthesis

1.1 General Remarks

All commercial reagents were used without further purification. Solvents were dried with the appropriate desiccants and distilled prior to use. Bruker Avance (400 MHz) and Varian (600 MHz) spectrometers were used to measure $^1$H and $^{13}$C NMR spectra employing 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, THF-d$_8$: $\delta_H$ 1.72 ppm, 3.58 ppm, $\delta_C$ 25.3 ppm, 67.2 ppm). The following abbreviations were used to describe 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. The 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 the 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 Varian 1000 FT-IR instrument. Elemental analysis was performed using the EA-3000 CHNS analyzer. UV-vis spectra were recorded on a Cary Win 50 (298 K) spectrometer. 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 multi-component assembly of rotors was performed directly in the NMR tube with CD$_2$Cl$_2$ as solvent. Compounds 1, 6, 7, A were synthesized according to literature known procedures.

![Scheme S1](image)

**Scheme S1.** Compounds 2-4 used in the model self-sorting and compound 5 used as internal standard in catalysis.
1.2 Synthesis of stators, rotators and nanoswitches

Zinc(II)-meso-5,15-bis-[4-(2-(4-bromo-2,3,5,6-tetramethylphenyl)-9-(2,4,6-trimethylphenyl)-[1,10]phenanthroline-3-ethinyl]phenyl]-10,20-bis-(2,4,6-trimethyl phenyl)porphyrin (S).

In an oven-dried 100 mL sealed tube, a mixture of 2-(2,3,5,6-tetramethyl-4-bromophenyl)-3-ethynil-9-(2,4,6-trimethylphenyl)-1,10-phenanthroline (6) (150 mg, 281 μmol) and meso-5,15-bis(mesityl)-10,20-bis(4-iodophenyl)porphyrin (7) (100 mg, 98.6 μmol) was dissolved in dry benzene (20 mL) and Et₂NH (20 mL). After thorough degassing, Pd(PPh₃)₄ (30.0 mg, 26.0 μmol) was added and the mixture was refluxed at 80 ºC for 12 h for completion of the coupling reaction. The reaction mixture was cooled down to room temperature and the solvents were removed. The residue was subjected to column chromatography (silica gel, CH₂Cl₂, Rf = 0.3) to afford 120 mg of ligand S as violet solid (65.7 μmol, 67%). **Melting point:** >300 ºC; **IR (KBr):** ν = 3441, 2963, 2914, 2733, 2362, 2201, 1913, 1804, 1701, 1602, 1491, 1442, 1263, 1162, 1093, 994, 846, 802, 765, 722, 573 cm⁻¹; **¹H NMR (400 MHz, CDCl₃):** δ = 8.85 (d, 4H, 3J = 4.6 Hz, β₁-H), 8.79 (d, 4H, 3J = 4.6 Hz, β₂-H), 8.63 (s, 2H, 4'-H), 8.33 (d, 3J = 8.4 Hz, 2H, 7'-H), 8.17 (d, 3J = 8.0 Hz, 4H, 15'-H), 7.95 (d, 2H, 3J = 9.0 Hz, 6'/5'-H), 7.92 (d, 3J = 9.0 Hz, 2H, 5'/6'-H), 7.61 (d, 3J = 8.4 Hz, 2H, 8'-H), 7.49 (d, 3J = 8.0 Hz, 4H, 14'-H), 7.29 (s, 4 H, 17'-H), 6.96 (s, 4 H, 9'-H), 2.64 (s, 6H, 18'-H), 2.53 (s, 12H, 12'-H), 2.33 (s,
6H, 11´-H), 2.16 (s, 12H, 13´-H), 2.13 (s, 12H, 10´-H), 1.83 (s, 12H, 16´-H); $^{13}$C NMR (100 MHz CDCl$_3$): $\delta =$ 162.6, 160.7, 150.0, 149.7, 144.7, 143.4, 139.2, 139.2, 138.9, 138.5, 137.9, 137.6, 137.5, 136.1, 136.0, 134.5, 133.8, 133.7, 132.1, 131.0, 129.7, 129.3, 128.5, 127.7, 127.7, 127.2, 127.0, 125.7, 125.2, 121.8, 120.2, 119.6, 119.3, 95.7, 87.8, 21.6, 21.5, 21.1, 21.0, 20.5, 18.7; ESI-MS: $m/z$ (%) = 1825.6 (60) [M+H]$^+$, 913.4 (100) [M+2H]$^{2+}$; UV-Vis: $\lambda_{abs}$ (CH$_2$Cl$_2$) = 422, 549, 595 nm; $\varepsilon_{422} = 2.17 \times 10^4$ M$^{-1}$cm$^{-1}$; Elemental analysis: (C$_{116}$H$_{94}$Br$_2$N$_8$Zn): calculated: C 76.33; H. 5.19; N. 6.14; found: C 76.32; H. 5.10; N. 5.92.

Spectroscopic data for nanoswitch 1

The preparation was executed as described earlier. Melting point: 165-168 °C; IR (KBr): $\tilde{\nu} =$ 3052, 2993, 2916, 2862, 2280, 2200, 1950, 1922, 1810, 1697, 1600, 1582, 1540, 1500, 1479, 1436, 1385, 1350, 1265, 1214, 1166, 1139, 1095, 1012, 952, 842, 756, 627, 585 cm$^{-1}$; $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta =$ 8.68 (ddd, $^3$J = 4.8 Hz, $^4$J = 1.2 Hz, $^5$J = 1.2 Hz, 1H, a-H), 8.54 (dt, $^3$J = 8.0 Hz, $^4$J = 1.2 Hz, $^5$J = 1.2 Hz, 1H, d-H), 8.33 (d, $^3$J = 8.0 Hz, 1H, 4-H), 8.32 (d, $^3$J = 8.0 Hz, 1H, 7-H), 8.23 (d, $^3$J = 8.4 Hz, 1H, c-H), 7.95 (d, $^3$J = 8.4 Hz, 1H, f-H), 7.90 (s, 2H, 5-, 6-H), 7.78 (td, $^3$J = 8.0 Hz, $^4$J = 1.2 Hz, 1H, c-H), 7.70-7.72 (m, 1H, s-H), 7.61-7.67 (m, 3H, j-, m-, p-H), 7.56 (d, $^3$J = 8.0 Hz, 1H, 3-H), 7.54 (s, 4H, n-, o-H), 7.52 (d, $^3$J = 8.0 Hz, 1H, 8-H), 7.40-7.46 (m, 2H, q-, r-H), 7.33-7.39 (m, 2H, k-, l-H), 7.21 (dddd, $^3$J = 8.0 Hz, $^4$J = 4.8 Hz, $^5$J = 1.2 Hz, 1H, b-H), 6.95 (s, 2H, 9-, 10-H), 5.57 (t, $^3$J = 2.0 Hz, 2H, g-H), 4.32 (t, $^3$J = 2.0 Hz, 2H, h-H), 4.06 (s, 5H, i-H), 2.56 (s, 6H, 14-H), 2.32 (s, 3H, 11-H), 2.03 (s, 6H, 12-H), 1.91 (s, 6H, 13-H) ppm; $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): $\delta =$ 161.3, 160.5, 159.1, 156.0, 154.6, 149.4, 146.6, 146.6, 142.8, 142.1, 138.4, 137.7, 137.0, 136.7, 136.4, 136.3, 136.0, 132.7, 132.6, 132.4, 132.2, 132.1, 132.1, 132.0, 128.8, 128.8, 128.7, 128.5, 128.1, 127.6, 127.5, 126.7, 126.6, 126.4, 125.9, 125.6, 124.9, 124.9, 124.7, 124.1, 123.7, 123.2, 123.0, 121.4, 117.0, 115.9, 95.8, 95.0, 93.6, 93.5, 93.2, 92.9, 91.0, 90.4, 84.0, 70.3, 70.1, 70.0, 21.2, 20.4, 18.7, 17.7 ppm. ESI-MS: $m/z$ (%) = 1093.4 (100) [I+H]$^+$; Elemental analysis: (C$_{77}$H$_{56}$FeN$_4$•0.5CH$_3$COOEt): Calculated: C, 83.59; H, 5.15; N, 4.94; Found: C, 83.27; H, 5.17; N, 5.00.
Spectroscopic data for rotator R

The full synthesis of rotator R will be presented in a follow-up publication soon. Below, we provide the full characterization of R. Melting point: 210-212 °C; IR (KBr): $\tilde{\nu}$ = 3050, 2923, 2211, 1593, 1569, 1537, 1489, 1478, 1404, 1375, 1315, 1214, 1090, 1066, 1014, 988, 936, 919, 820, 795, 748, 686, 646, 587, 565, 544, 533, 497 cm$^{-1}$; $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ = 8.61 (d, $^3J$ = 6.0 Hz, 4H, a’-H), 7.74 (t, $^4J$ = 1.6 Hz, 2H, f’-H), 7.57 (dt, $^3J$ = 8.0 Hz, 4H, e’/c’-H), 7.52 (dt, $^3J$ = 8.0 Hz, $^4J$ = 1.6 Hz, 2H, c’/e’-H), 7.40 (d, $^3J$ = 6.0 Hz, 4H, d’-H), 7.38 (t, $^3J$ = 8.0 Hz, 2H, d’-H), 2.51 (s, 12H, g’-H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 149.8, 135.8, 134.4, 131.9, 131.3, 131.1, 128.6, 125.5, 124.3, 123.2, 122.5, 97.1, 93.1, 89.5, 87.2, 18.4 ppm; ESI-MS: m/z (%) 537.4 (100) [R + H]$^+$; Elemental analysis: Calculated: (C$_{40}$H$_{28}$N$_2$•H$_2$O): C, 86.61; H, 5.45; N, 5.05; Found: C, 86.47; H, 5.06; N, 4.70.

2. Synthesis and characterization of complexes

All solid compounds were placed in an NMR tube and then dissolved in CD$_2$Cl$_2$. Subsequently NMR spectra were measured at 298 K. Zn(OTf)$_2$ was added as a standard solution in CD$_3$CN.

Complex C1 = [Cu(3)(4)]$^+$

In an NMR tube, 2,9-dimesityl-[1,10]-phenanthroline (3) (0.592 mg, 1.42 µmol), 6-ferrocenyl-2,2’-bipyridine (4) (0.483 mg, 1.42 µmol), and [Cu(CH$_3$CN)$_4$]PF$_6$ (0.530 mg, 1.42 µmol) were dissolved in 500 µL of CD$_2$Cl$_2$. Yield by NMR: quantitative; $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ = 8.57 (d, $^3J$ = 8.8 Hz, 2H, 4-, 7-H), 8.10 (s, 2H, 5-, 6-H), 7.95 (dd, $^3J$ = 4.8 Hz, $^4J$ = 1.6 Hz, 1H, a-H), 7.85 (td, $^3J$
= 8.0 Hz, $^4J = 1.6$ Hz, 1H, c-H), 7.79 (d, $^3J = 8.0$ Hz, 1H, d-H), 7.78 (t, $^3J = 8.0$ Hz, 1H, f-H), 7.77 (d, $^3J = 8.8$ Hz, 2H, 3-, 8-H), 7.65 (d, $^3J = 8.0$ Hz, 1H, g-H), 7.33 (d, $^3J = 8.0$ Hz, 1H, e-H), 7.27 (ddd, $^3J = 8.0$ Hz, $^3J = 4.8$ Hz, $^4J = 1.6$ Hz, 1H, b-H), 6.40 (s, 2H, 9/9´-H), 6.37 (s, 2H, 9/9´-H), 4.06 (bvs, 2H, Fe-H), 3.82 (bvs, 5H, Fe-H), 3.44 (bvs, 2H, Fe-H), 2.00 (s, 6H, 11+11´-H), 1.82 (s, 6H, 10/10´-H), 1.77 (s, 6H, 10/10´-H) ppm; ESI-MS: m/z (%) = 819.9 (100) [[Cu(3)(4)]$^{+}$].

Complex C2 = [Zn(3)(4)]$^{2+}$

In an NMR tube 3 (0.662 mg, 1.59 µmol), 4 (0.540 mg, 1.59 µmol) were dissolved in 500 µL of CD$_2$Cl$_2$. NMR spectra were measured immediately after addition of Zn(OTf)$_2$ (0.578 mg, 1.59 µmol) as a standard solution in CD$_3$CN. Yield: quantitative. $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ = 9.04 (d, $^3J = 8.8$ Hz, 2H, 4-, 7-H), 8.41 (s, 2H, 5-, 6-H), 8.36 (d, $^3J = 4.6$ Hz, 1H, a-H), 8.31 (td, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, 1H, c-H), 8.25 (dd, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, 1H, d-H), 8.19 (t, $^3J = 8.0$ Hz, 1H, f-H), 8.12 (dd, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, 1H, g-H), 8.08 (d, $^3J = 8.8$ Hz, 2H, 3-, 8-H), 8.05 (dd, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, 1H, b-H), 6.39 (s, 2H, 9/9´-H), 6.25 (s, 2H, 9/9´-H), 4.05 (bvs, 2H, Fe-H), 3.97 (bvs, 5H, Fe-H), 3.78 (bvs, 2H, Fe-H), 1.91 (s, 6H, 11-, 11´-H), 1.76 (s, 6H, 10/10´-H), 1.70 (s, 6H, 10/10´-H) ppm; ESI-MS: m/z (%) = 969.6 (100) [[Zn(3)(4)+OTf$^-$]$^{+}$].
Complex C3 = [(S)•(R)]

In an NMR tube, stator S (1.08 mg, 0.592 µmol) and rotator R (0.318 mg, 0.592 µmol) were dissolved in 500 µL of CD₂Cl₂. The NMR spectrum suggested full conversion.Mp > 250 °C; IR (KBr): \( \tilde{\nu} = 3027, 2917, 2210, 1596, 1489, 1458, 1381, 1336, 1263, 1203, 1063, 995, 896, 849, 796, 721, 684, 638, 623, 543 \text{ cm}^{-1} \); \(^1\)H NMR (400 MHz, CD₂Cl₂): 8.79 (d, 4H, \(^3J = 4.8\) Hz, \(\beta_1\)-H), 8.70 (d, 4H, \(^3J = 4.8\) Hz, \(\beta_2\)-H), 8.65 (s, 2H, 4'-H), 8.36 (d, \(^3J = 8.4\) Hz, 2H, 7'-H), 8.14 (d, \(^3J = 8.0\) Hz, 4H, 15'-H), 7.98 (d, 2H, \(^3J = 9.0\) Hz, 6'/5'-H), 7.95 (d, \(^3J = 9.0\) Hz, 2H, 5'/6'-H), 7.59 (d, \(^3J = 8.4\) Hz, 2H, 8'-H), 7.55 (t, \(^4J = 1.6\) Hz, 2H, f'-H), 7.50 (d, \(^3J = 8.0\) Hz, 4H, 14'-H), 7.50 (1H, c'-H merged with 14'-H), 7.34 (dt, \(^3J = 7.8\) Hz, \(^4J = 1.6\) Hz, 2H, e'-H), 7.31 (t, \(^3J = 7.8\) Hz, 2H, d'-H), 7.29 (s, 4H, 17'-H), 6.97 (s, 4H, 9'-H), 6.58 (brs, 4H, b'-H), 5.71 (brs, 4H, a'-H), 2.62 (s, 6H, 18'-H), 2.54 (s, 12H, 12'-H), 2.44 (s, 12H, g'-H), 2.34 (s, 6H, 11'-H), 2.13 (s, 12H, 13'-H), 2.07 (s, 12H, 10'-H), 1.81 (s, 12H, 16'-H); UV-Vis: \( \lambda_{abs} (\text{CH}_2\text{Cl}_2) = 426, 553, 599 \text{ nm}; \epsilon_{426} = 2.11 \times 10^4 \text{ M}^{-1}\text{cm}^{-1} \); Elemental analysis: (C\(_{156}\)H\(_{122}\)Br\(_2\)N\(_{10}\)Zn• 2H\(_2\)O): Calculated: C, 78.14; H, 5.30; N, 5.84. Found: C, 78.22; H, 4.94; N, 5.75.

Complex C4 = [Cu\(_2\)(S)(R)]\(^{2+}\)

Complex C3 = [(S)•(R)]
In an NMR tube, [Cu(CH3CN)4]PF6 (0.422 mg, 1.13 µmol), stator S (1.03 mg, 0.564 µmol), and rotator R (0.302 mg, 0.564 µmol) were dissolved in 500 µL of CD2Cl2. The NMR spectrum indicated quantitative formation of the nanorotor [Cu2(S)(R)]2+. 

**Mp > 250 °C; IR (KBr):** \( \tilde{\nu} = 3036, 2919, 2209, 1605, 1491, 1459, 1382, 1364, 996, 843, 796, 719, 683, 623, 560 \text{ cm}^{-1} \); 

**1H NMR (400 MHz, CD2Cl2):** 8.95 (s, 2H, 4´-H), 8.80 (d, 4H, \( ^3J = 4.4 \text{ Hz, } \beta_1\)-H), 8.76 (d, \( ^3J = 8.4 \text{ Hz, } 2\text{H, } 7´\)-H), 8.74 (d, 4H, \( ^3J = 4.4 \text{ Hz, } \beta_2\)-H), 8.26 (d, 2H, \( ^3J = 8.8 \text{ Hz, } 6´/5´\)-H), 8.23 (d, \( ^3J = 8.8 \text{ Hz, } 2\text{H, } 5´/6´\)-H), 8.15 (d, \( ^3J = 7.8 \text{ Hz, } 4\text{H, } 15´\)-H), 7.98 (d, \( ^3J = 8.4 \text{ Hz, } 2\text{H, } 8´\)-H), 7.69 (brs, 2H, f´-, f´´-H), 7.56 (d, \( ^3J = 7.8 \text{ Hz, } 2\text{H, } e´-, e´´-H), 7.47 (d, \( ^3J = 7.8 \text{ Hz, } 2\text{H, } c´-, c´´-H), 7.36-7.42 (m, 6H, d´-, d´´-, 14´-H), 7.29 (s, 4H, 17´-H), 7.03 (s, 4H, 9´-H), 6.89 (brs, 4H, b´-H), 5.66 (brs at −60 °C, 4H, a´-H), 2.61 (s, 6H, 18´-H), 2.43 (s, 12H, g´-H), 2.13 (s, 12H, 12´-H), 2.38 (s, 6H, 11´-H), 2.14 (s, 12H, 13´-H), 2.10 (s, 12H, 10´-H), 1.79 (s, 12H, 16´-H); 

**ESI-MS:** \( m/z (\%) = 1244.7 (100) \); 

**UV-Vis:** \( \lambda_{\text{abs}} (\text{CH}_2\text{Cl}_2) = 429, 559, 602, 607 \text{ nm}; \; \varepsilon_{429} = 1.96 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}; \)** 

**Elemental analysis:** (C156H122Br2Cu2F12N10P2Zn): Calculated: C, 67.42; H, 4.43; N, 5.04. Found: C, 67.50; H, 4.41; N, 5.26.

**Complex C5:** \([\text{Cu}(1)]^+\)

Switch 1 (0.770 mg, 0.704 µmol) and [Cu(CH3CN)4]PF6 (0.263 mg, 0.705 µmol) were placed into an NMR tube. To this mixture, 500 µL of CD2Cl2 was added and subsequently the NMR was recorded. **Yield:** Quantitative; 

**1H NMR (400 MHz, CD2Cl2):** \( \delta = 8.65 (d, \; ^3J = 8.0 \text{ Hz, } 1\text{H, } 7/4\text{-H}), 8.63 (d, \; ^3J = 8.0 \text{ Hz, } 1\text{H, } 4/7\text{-H}), 8.19 (s, 2\text{H, } 5\text{-}, 6\text{-H}), 8.03 (dd, \; ^3J = 4.6 \text{ Hz, } ^4J = 1.2 \text{ Hz, } 1\text{H, } a\text{-H}), 7.80 (td, \; ^3J = 8.0 \text{ Hz, } ^4J = 1.2 \text{ Hz, } 1\text{H, } c\text{-H}), 7.77 (d, \; ^3J = 8.0 \text{ Hz, } 2\text{H, } 3\text{-}, 8\text{-H}), 7.66-7.72 (m, 3\text{H, } d\text{-}, m\text{-}, p\text{-H}), 7.60-7.64 (m, 3\text{H, } g\text{-}, j\text{-}, f\text{-H}), 7.51 (s, 4\text{H, } k\text{-}, l\text{-H}), 7.46-7.48 (m, 2\text{H, } n\text{-}, o\text{-H}), 7.40-7.42 (m, 2\text{H, } h\text{-}, i\text{-H}), 7.31 (ddd, \; ^3J = 8.0 \text{ Hz, } ^3J = 4.8 \text{ Hz, } ^4J = 1.2 \text{ Hz, } 1\text{H, } b\text{-H}), 7.29 (d, \; ^3J = 8.4 \text{ Hz, } 1\text{H, } e\text{-H}), 6.43 (s, 1\text{H, } 10/9\text{-H}), 6.35 (s, 1\text{H, } 9/10\text{-H}), 4.92 (bs, 1\text{H, } Fc\text{-H}), 4.54 (bs, 1\text{H, } Fc\text{-H}), 3.89 (bs, 5\text{H, Fc-H}), 3.67 (bs, 1\text{H, Fc-H}), 3.32 (bs, 1\text{H, Fc-H}), 2.17 (s, 3\text{H, duMe-H}), 1.97 (s, 3\text{H, mesMe-H}), 1.68 (s, 3\text{H, duMe-H}), 1.78 (s, 3\text{H, mesMe-H}), 1.73 (s, 3\text{H, duMe-H}), 1.65 (s, 3\text{H, mesMe-H}), 1.53 (s, 3\text{H, duMe-H}) ppm; 

**ESI-MS:** \( m/z (\%) = 1156.3 (100) \); 

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Complex $C6^1 = [Zn(1)]^{2+}$

In an NMR tube, ligand $1$ (0.613 mg, 0.561 μmol) was dissolved in 425 μL of CD$_2$Cl$_2$. Thereafter, Zn(OTf)$_2$ (0.204 mg, 0.562 μmol) was added as a standard solution in CD$_3$CN. Subsequently, $^1$H NMR was measured without purification. **Yield:** Quantitative; $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN (5:1)): $\delta = 9.12$ (d, $^3J = 8.4$ Hz, 1H, 7/4-H), 8.92 (d, $^3J = 8.4$ Hz, 1H, 4/7-H), 8.71 (d, $^3J = 5.2$ Hz, 1H, a-H), 8.45 (d, $^3J = 8.8$ Hz, 1H, 6/5-H), 8.39 (d, $^3J = 8.8$ Hz, 1H, 5/6-H), 8.20 (td, $^3J = 7.8$ Hz, $^4J = 1.2$ Hz, 1H, c-H), 8.17 (d, $^3J = 8.4$ Hz, 1H, 8/3-H), 8.02 (d, $^3J = 8.0$ Hz, 1H, d-H), 7.93 (d, $^3J = 8.4$ Hz, 1H, 3/8-H), 7.89 (d, $^3J = 8.4$ Hz, 1H, f-H), 7.81-7.83 (m, 1H, p-H), 7.74 (ddd, $^3J = 7.8$ Hz, $^3J = 5.2$ Hz, $^4J = 1.2$ Hz, 1H, b-H), 7.63-7.67 (m, 3H, g-, j-, m-H), 7.62 (s, 4H, k-, l-H), 7.58 (d, $^3J = 8.4$ Hz, 1H, e-H), 7.54-7.56 (m, 2H, h-, i-H), 7.44-7.46 (m, 2H, n-, o-H), 6.43 (s, 1H, 10/9-H), 6.03 (s, 1H, 9/10-H), 5.48 (ddd, $^3J = 2.8$ Hz, $^4J = 1.2$ Hz, $^5J = 0.4$ Hz, 1H, Fc-H), 4.37 (td, $^3J = 2.8$ Hz, $^4J = 1.2$ Hz, 1H, Fc-H), 3.98 (s, 5H, Fc-H), 3.84 (ddd, $^3J = 2.8$ Hz, $^4J = 1.2$ Hz, $^5J = 0.4$ Hz, 1H, Fc-H), 3.35 (td, $^3J = 2.8$ Hz, $^4J = 1.2$ Hz, 1H, Fc-H), 2.22 (s, 3H, mesMe-H), 1.89 (s, 3H, duMe-H), 1.86 (s, 6H, duMe-H), 1.83 (s, 3H, mesMe-H), 1.71 (s, 3H, duMe-H), 1.53 (s, 3H, mesMe-H), ppm; **ESI-MS:** $m/z$ (%) = 578.2 (35) [Zn(1)]$^{2+}$, 1307.2 (100) [Zn(1)+OTf]$^+$.

### 3. Model Study

Metal-ion dependent self-sorting was tested by mixing $2$, $3$, $4$, and [Cu(CH$_3$CN)$_4$]PF$_6$ (1.23 μmol) in a ratio of 1:2:1:1 in CD$_2$Cl$_2$. The subsequently measured $^1$H NMR spectrum was compared with those of the individual complexes. The heteroleptic copper complex [Cu(3)(4)]$^+$ formed selectively. After addition of 1.0 equiv. of Zn(OTf)$_2$ (as a standard solution in CD$_3$CN), complexes [Zn(3)(4)]$^{2+}$ and [Cu(2)(3)]$^{2+}$ were afforded as judged by $^1$H NMR. The former complex simulates formation of nanoswitch [Zn(1)]$^{2+}$, whereas the latter represents a HETPYP binding motif (= N$_{py}$ → [Cu(phenAr$_2$)])$^+$, log $K = 3.2$),$^5$ which was used in nanorotor [Cu$_2$(S)(R)]$^{2+}$.
Finally the self-sorting scenario and the translocation was tested by mixing 1, 2, 3 and [Cu(CH$_3$CN)$_4$]PF$_6$ (1.27 μmol) in a ratio of 1:1:1:1 in CD$_2$Cl$_2$. Subsequently, the $^1$H NMR was measured and compared with those of the individual complexes. Accordingly, the copper complex [Cu(I)]$^+$ was afforded selectively whereas 2 and 3 remain free in the solution. After addition of 1.0 equiv. of Zn(OTf)$_2$ (as a standard solution in CD$_3$CN) complexes [Zn(I)]$^{2+}$ and [Cu(2)(3)]$^+$ were furnished as judged by $^1$H NMR comparison. Thus translocation of Cu(I) was confirmed.
Figure S2. $^1$H NMR (400 MHz, 298 K) of (a) complex $[Cu(1)]^+$; (b) after mixing of 1, 2, 3 and $[Cu(CH_3CN)_4]PF_6$ in a ratio of 1:1:1:1 in CD$_2$Cl$_2$; (c) after addition of Zn(OTf)$_2$ to solution (b); (d) complex $[Zn(1)]^{2+}$ for comparison.
4. NMR spectra: $^1$H NMR, $^{13}$C NMR, $^1$H-$^1$H COSY

Figure S3. $^1$H NMR spectrum of stator S in CDCl$_3$ (400 MHz, 298 K).

Figure S4. $^1$H-$^1$H COSY spectrum of stator S in CDCl$_3$ (400 MHz, 298 K).
Figure S5. $^{13}$C NMR spectrum of stator S in CDCl$_3$ (100 MHz, 298 K).

Figure S6. $^1$H NMR spectrum of rotator ligand R in CD$_2$Cl$_2$ (400 MHz, 298 K).
**Figure S7.** $^{13}$C NMR spectrum of rotator R in CDCl$_3$ (100 MHz, 298 K).

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

Figure S10. $^1$H NMR spectrum of complex [Cu(3)(4)]$^+$ in CD$_2$Cl$_2$ (400 MHz, 298 K).
Figure S11. $^1$H-$^1$H COSY spectrum of [Cu(3)(4)]$^+$ in CD$_2$Cl$_2$ (400 MHz, 298 K).

Figure S12. $^1$H NMR spectrum (400 MHz, 298 K) of complex [Zn(3)(4)]$^{2+}$ in CD$_2$Cl$_2$:CD$_3$CN (9:1).
Figure S13. $^1$H-$^1$H COSY spectrum (400 MHz, 298 K) of $[\text{Zn}(3(4))^{2+}$ in CD$_2$Cl$_2$:CD$_3$CN (9:1).

Figure S14. $^1$H NMR spectrum (400 MHz, 298 K) of complex $[(S)(R)]$ in CD$_2$Cl$_2$. 

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Figure S15. $^1$H-$^1$H COSY spectrum (400 MHz, 298 K) of complex [(S)(R)] in CD$_2$Cl$_2$. 
Figure S16. $^1$H NMR spectrum (400 MHz, 298 K) of complex $[\text{Cu}_2(\text{S})(\text{R})]^2^+\text{in CD}_2\text{Cl}_2$.

Figure S17. $^1$H-$^1$H COSY spectrum (400 MHz, 298 K) of complex $[\text{Cu}_2(\text{S})(\text{R})]^2^+\text{in CD}_2\text{Cl}_2$. 
Figure S18. $^1$H NMR spectrum (400 MHz, 298 K) of complex [Cu(1)]$^+$ in CD$_2$Cl$_2$.

Figure S19. $^1$H NMR spectrum (400 MHz, 298 K) of complex [Zn(1)]$^{2+}$ in CD$_2$Cl$_2$-CD$_3$CN (5:1).
**Figure S20.** $^1$H NMR spectrum (400 MHz, 298 K) of (a) complex $[\text{Cu(I)}]^+$ in CD$_2$Cl$_2$, (b) after addition of 60 µL of CD$_3$CN to the same complex. Now mesityl protons 9-H and 10-H show up as a broad singlet at 6.36 ppm.

**Figure S21.** Partial $^1$H NMR (400 MHz, in CD$_2$Cl$_2$) of (a) $[\text{Zn(I)}]^2+$; (b) NetState II: mixture of $[\text{Cu}_2(\text{S})(\text{R})]^2+$ and $[\text{Zn(I)}]^2+$; (c) NetState I: mixture of $[\text{Cu(I)}]^+$ and $[(\text{S})(\text{R})]$. (d) $[\text{Cu(I)}]^+$; (e) $[\text{Cu}_2(\text{S})(\text{R})]^2+$; (f) $[(\text{S})(\text{R})]$. 

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Figure S22. \textsuperscript{1}H NMR spectra (400 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 298 K) showing the reversible switching between \textbf{NetState I} and \textbf{II} over 2 cycles. The different NMR traces represent: (a) after mixing of switch \textbf{1}, \textbf{S}, \textbf{R} and [Cu(CH\textsubscript{3}CN)\textsubscript{4}]PF\textsubscript{6} (1.8 \times 10^{-3} M) in 2:1:1:2 ratio (\textbf{NetState I}); (b) after adding 2.0 equiv. of Zn(OTf\textsubscript{2}) as a standard solution in CD\textsubscript{3}CN, furnishing [Zn(1)]\textsuperscript{2+} and [Cu\textsubscript{2}(S)(R)]\textsuperscript{2+} (\textbf{NetState II}); (c) NMR after addition of 2.0 equiv. of hexacyclen to produce \textbf{NetState I}; (d) after adding another 2.0 equiv. of Zn(OTf\textsubscript{2}) (\textbf{NetState II}); (e) NMR after addition of 2.0 equiv. of hexacyclen; (f) after adding another 2.0 equiv. of Zn(OTf\textsubscript{2}) (\textbf{NetState II}); (g) NMR after addition of 2.0 equiv. of hexacyclen. Blue asterisk marked signals are from [Zn(hexacyclen)]\textsuperscript{2+} complex.
Mechanism of metal translocation
Figure S23. $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1) of the Cu$^+$ translocation at 298 K ($8.9 \times 10^{-4}$ M). To a solution of NetState I in CD$_2$Cl$_2$ in an NMR tube was added Zn(OTf)$_2$ as a standard solution in CD$_3$CN. Subsequently, $^1$H NMR spectra were recorded to elucidate the metal exchange at nanoswitch I with time.

5. Catalytic experiments

Solid reactants were transferred to the NMR tube and dissolved in CD$_2$Cl$_2$:CD$_3$CN = 5:1. The mixture was heated at 50 °C for 2 h and the yield of the click (singlet at δ 5.98 ppm) was determined using 1,3,5-trimethoxybenzene (5) as an internal standard (singlet at δ 6.04 ppm).
Figure S24. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained after heating the reaction mixture of ($\approx$ 1.92 mM) [Cu(CH$_3$CN)$_4$]PF$_6$, A, B and trimethoxybenzene 5 in 1:10:50:10 ratio at 50 °C for 2 h. The integration demonstrated that AB was formed in 26% yield.

Figure S25. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained after heating the reaction mixture of stator S ($\approx$ 0.96 mM), rotator R, [Cu(CH$_3$CN)$_4$]PF$_6$, A, B and trimethoxybenzene 5 in 1:1:2:20:100:20 ratio at 50 °C for 2 h. The integration demonstrated that AB was formed in 37% yield.
Figure S26. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained after heating the reaction mixture of nanoswitch 1 (≈ 1.92 mM), [Cu(CH$_3$CN)$_4$]PF$_6$, A, B and trimethoxybenzene 5 in 1:1: 10:100:10 ratio at 50 °C for 2 h does not show any product AB.

Figure S27. Partial $^1$H-NMR (400 MHz, CD$_2$Cl$_2$, 298 K) of (a) [(S)+$(R)]$, (b) nanorotor [Cu$_2$(S)$(R)]^{2+}$, (c) mixture of nanorotor [Cu$_2$(S)$(R)]^{2+}$ and click product AB in 1: 10 ratio.
Figure S28a. Run 1 with two catalytic cycles. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained after (a) heating the reaction mixture of 1 ($\approx$ 1.92 mM), S, R, [Cu(CH$_3$CN)$_4$]PF$_6$, A, B, 5 in a 2:1:2:2:20:100:20 ratio at 50 °C for 2 h in an NMR tube revealed that click catalysis (no singlet at $\delta$ 5.98) was OFF. (b) After addition of 2.0 equiv. of Zn(OTf)$_2$ with respect to S and subsequent heating at 50 °C for 2 h click product AB was formed (yield = 36% calculated with respect to internal standard 5). (c) After adding 2.0 equiv. of hexacyclen with respect to S and heating at 50 °C for 2 h, only 2% increase in the amount of click product AB was observed (yield = 38%). (d) After addition of 2.0 equiv. of Zn(OTf)$_2$ with respect to S and heating at 50 °C for 2 h resulted in an increase of the click product AB by 33% (total yield = 71%). (e) After adding 2.0 equivalent of hexacyclen with respect to S and heating at 50 °C for 2 h, only 1% increase in the amount of click product AB was observed (total yield = 72%).
Figure S28b. Run 2 with two catalytic cycles. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained after (a) heating the reaction mixture of 1 (≈ 1.92 mM), S, R, [Cu(CH$_3$CN)$_4$]PF$_6$, A, B, 5 in a 2:1:1:2:20:100:20 ratio at 50 °C for 2 h in an NMR tube revealed that click catalysis (no singlet at δ 5.98) was OFF. (b) After addition of 2.0 equiv. of Zn(OTf)$_2$ with respect to S and subsequent heating at 50 °C for 2 h click product AB was formed (yield = 36% calculated with respect to internal standard 5). (c) After adding 2.0 equiv. of hexacyclen with respect to S and heating at 50 °C for 2 h, only 1% increase in the amount of click product AB was observed (yield = 37%). (d) After addition of 2.0 equiv. of Zn(OTf)$_2$ with respect to S and heating at 50 °C for 2 h resulted in an increase of the click product AB by 38% (total yield = 75%).
Figure S28c. Run 3 with two catalytic cycles. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained after (a) heating the reaction mixture of 1 ($\approx$ 1.92 mM), S, R, [Cu(CH$_3$CN)$_4$]PF$_6$, A, B, 5 in a 2:1:1:2:20:100:20 ratio at 50 °C for 2 h in an NMR tube revealed that click catalysis (no singlet at $\delta$ 5.98) was OFF. (b) After addition of 2.0 equiv. of Zn(OTf)$_2$ with respect to S and subsequent heating at 50 °C for 2 h click product AB was formed (yield = 35% calculated with respect to internal standard 5). (c) After adding 2.0 equiv. of hexacyclen with respect to S and heating at 50 °C for 2 h, only 2% increase in the amount of click product AB was observed (yield = 37%). (d) After addition of 2.0 equiv. of Zn(OTf)$_2$ with respect to S and heating at 50 °C for 2 h resulted in an increase of the click product AB by 37% (total yield = 74%).
Figure S29. $^1$H NMR (400 MHz, CD$_2$Cl$_2$:CD$_3$CN = 5:1, 298 K) spectrum obtained (a) after heating the reaction mixture of nanoswitch 1 ($\approx$ 1.92 mM), [Cu(CH$_3$CN)$_4$]PF$_6$, A, B and trimethoxybenzene 5 in 1:1:10:100:10 ratio at 50 °C for 2 h does not show any product AB. (b) After addition of 1.0 equiv. of Zn(OTf)$_2$ as a standard solution in CD$_3$CN followed by heating at 50 °C for 2 h, the yield of AB is 26%.

6. DOSY NMR spectra

Calculation of hydrodynamic radius from:

a) DOSY: The diffusion coefficient $D$ for [Zn(S)(R)]$^{2+}$ and [Cu(S)(R)]$^+$ was obtained from their DOSY spectrum. The corresponding hydrodynamic radius was calculated by using the Stokes-Einstein equation

$$r = \frac{k_BT}{6\pi\eta D}$$
b) **Optimized structure:** Radius of $[\text{Zn(S)(R)}]^ {2+}$ was calculated from their optimized structures at PM6 level. First a circle around the structure was considered and its radius approximated as hydrodynamic radius of the rotor. It is denoted as $r_{\text{com}}$.

![Figure S30. $^1$H-DOSY NMR of $[\text{Cu}_2(\text{S}(\text{R}))]^ {2+}$ in CD$_2$Cl$_2$ (600 MHz, 298K). Diffusion coefficient $D = 3.6 \times 10^{-10}$ m$^2$ s$^{-1}$, Hydrodynamic radius $r \sim 14.7$ Å.](image-url)
Figure S31. $^1$H-DOSY NMR of [(S)•(R)] in CD$_2$Cl$_2$ (600 MHz, 298K). Diffusion coefficient $D = 4.3 \times 10^{-10}$ m$^2$ s$^{-1}$, Hydrodynamic radius $r \sim 12.3$ Å.
7. Variable temperature studies and determination of kinetic parameters

**Figure S32.** (a) Partial $^1$H VT-NMR (CD$_2$Cl$_2$, 600 MHz) of [Cu$_2$(S)(R)]$^{2+}$ shows the splitting of proton 4’-H (red asterisk marked) in aromatic region. Upon lowering the temperature proton 4’-H splits into two sets in 1:1 ratio. (b) Experimental and theoretical splitting of proton 4’-H with exchange frequency at different temperature. (c) Eyring plot for the exchange dynamics in nanorotor [Cu$_2$(S)(R)]$^{2+}$.

$$y = -5.91x + 24.9$$
$$R^2 = 0.99$$

$$\Delta H^\ddagger = \pm 49.1 \text{ kJ mol}^{-1}$$
$$\Delta S^\ddagger = 9.5 \pm 1.7 \text{ J mol}^{-1} \text{ K}^{-1}$$
$$\Delta G^\ddagger_{298} = 46.6 \text{ kJ mol}^{-1}$$
8. ESI-MS Spectra

Figure S33. ESI-MS of rotator R after protonation.

Figure S34. ESI-MS of stator S after protonation.
Figure S35. ESI-MS of complex C1.

Figure S36. ESI-MS of complex C2.
Figure S37. ESI-MS of complex C4.

Figure S38. ESI-MS of complex C5.
Figure S39. ESI-MS of complex C6.

Figure S40. ESI-MS of NetState I.
Figure S41. ESI-MS of NetState II.

9. UV-Vis data

Figure S42. UV-vis spectra of stator S, pre-rotor [(S)(R)] and nanorotor [Cu₂(S)(R)²⁺] in CH₂Cl₂ (10⁻⁵ M) at 298 K.
Measurement of Binding Constant:

**Figure S43.** UV-vis titration of $[\text{Cu}_2\text{(S)}]^+$ ($2.3 \times 10^{-5}$ M) vs. $R$ ($1.0 \times 10^{-3}$ M) in CH$_2$Cl$_2$ at 298 K. The binding constant was determined as $\log K = 7.13 \pm 0.28$ using SPECFIT software.

**Figure S44.** UV-vis titration of $[\text{Cu}(3)]^+$ ($7.1 \times 10^{-6}$ M) vs. $4$ ($1.4 \times 10^{-4}$ M) in CH$_2$Cl$_2$ at 298 K. The binding constant was determined as $\log K = 4.70 \pm 0.34$ using SPECFIT software.
Figure S45. UV-vis titration of $[Zn(3)]^{2+} \times 10^{-6}$ M vs. 4 $\times 10^{-4}$ M in CH$_2$Cl$_2$ at 298 K. The binding constant was determined as log $K = 7.43 \pm 0.61$ using SPECFIT software.

Figure S46. Change in UV-vis from NetState I (10$^{-5}$ M) to NetState II after metal-metal exchange.
10. Speciation analysis

The binding constant of Cu$^+$ to the pre-rotor [Cu(S)(R)]$^+$ is log $K \sim 5.1$. We derive the percentage of free copper(I) ions in solution from the speciation distribution curve. From the analysis at the given concentration, 94% of Cu$^+$ should be firmly bound to nanorotor [Cu$_2$(S)(R)]$^+$ (both used at $c = 1.92$ mM) and a maximum of 6% of Cu$^+$ is released into solution. From Figure S24 we derive that 100% of Cu$^+$ generate 26% yield of AB, thus 6% of Cu$^+$ may produce at most 1.6% of AB adding only insignificantly to the catalytic activity of the full system.

![Figure S47. Calculated species distribution between [Cu$_2$(S)(R)]$^{2+}$ and Cu$^+$ at different concentrations.](image)

11. References