Supporting Information

Reversible Interconversion of a Static Metallosupramolecular Cage Assembly into a High-Speed Rotor – Stepless Adjustment of Rotational Exchange by Nucleophile Addition

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Table of contents

1. Synthesis S2
   1.1 General Information S2
   1.2 Synthesis and Characterization of Ligands S3-5
   1.3 Characterization of Nanorotors S6-9

2. NMR spectra: $^1$H, $^{13}$C, $^1$H-$^1$H COSY S10-14
3. Titration of Nanorotor ROT-1 with CD$_3$CN, TBAI and PPh$_3$ S15-22
4. Variable Temperature $^1$H NMR Spectra S23-24
5. $^1$H-$^1$H ROESY NMR Spectra S25-31
6. DOSY NMR Spectra S32
7. ESI-MS Spectra S33
8. Measurement of Binding Constant S34
9. References S35

DDQ: 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone.
1. Synthesis

1.1 General Information

All solvents were dried by distillation prior to use while commercial reagents were utilized without any further purification. Bruker Advance (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$_3$: $\delta_H$ 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; CD$_3$CN: $\delta_H$ 1.32 ppm, $\delta_C$ 118.26 ppm). The following abbreviations were used to define NMR peak patterns: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublets of doublets, bs = broad singlet, m = multiplet. The coupling constant values are given in Hertz (Hz) and, wherever possible, assignment of protons is given. The numbering of carbons in different molecular skeletons does not necessarily follow IUPAC nomenclature rules; it is exclusively done for assigning NMR signals. ROESY spectra were obtained with 1.5 s relaxation delay and 300 ms mixing time. 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) using molecular weight calculator 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. 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). All rotor preparations were performed directly in the NMR tube using CD$_2$Cl$_2$, CD$_3$CN or a mixture of CD$_2$Cl$_2$ and CD$_3$CN as solvent.
1.2 Synthesis and characterization of ligands

Scheme S1. Synthetic route to rotator 1.

Synthesis of compounds 2, 4 and 6 was accomplished by literature known procedure.
5,10-Bis[4-(4'-pyridinylethynyl)phenyl]-15,20-dimesitylporphyrin (7)

Compound 6 (100 mg, 104 µmol), 4-vinylpyridine (88.5 mg, 1.04 mmol) and K₂CO₃ (286 mg, 2.07 mmol) were combined in a sealed tube under N₂ atmosphere with dry DMF (15 mL) and dry Et₃N (15 mL). The mixture was degassed by using two freeze-pump-thaw cycles. Then Pd(PPh₃)₄ (18.0 mg, 15.5 µmol) was added under N₂ atmosphere. After degassing again by freeze-pump-thaw cycles, P₃Bu₃HBF₄ (1.00 mg, 3.45 µmol) was added to the reaction mixture under N₂ atmosphere. After stirring at 70 ºC for 18 h, the solvent was evaporated. The residue was then worked up with ice cold water to remove DMF. The organic part was extracted with CH₂Cl₂, dried over anhydrous Na₂SO₄ and concentrated. The compound was purified by gel column chromatography (SiO₂) using 1% CH₃OH in CH₂Cl₂ as eluent to afford a purple solid (70.0 mg, 75%). \( R_f = 0.5 \) (SiO₂, 4% MeOH in CH₂Cl₂). mp: > 200 ºC.

IR (KBr): \( \nu = 733, 802, 957, 1188, 1218, 1347, 1384, 1414, 1471, 1594, 1712, 2849, 2917, 3026, 3324, 3436 \text{ cm}^{-1} \). \( ^1H \text{ NMR (CDCl}_3, 400 \text{ MHz)}: \delta = -2.54 \) (s, 2H, N-H), 1.89 (s, 12H, f-H), 2.65 (s, 6H, g-H), 7.31 (s, 4H, e-H), 7.34 (d, \( ^3J = 16.4 \text{ Hz} \), 2H, m-H), 7.52 (d, \( ^3J = 6.0 \text{ Hz} \), 4H, c-H), 7.64 (d, \( ^3J = 16.4 \text{ Hz} \), 2H, n-H), 7.93 (d, \( ^3J = 8.2 \text{ Hz} \), 4H, b-H), 8.25 (d, \( ^3J = 8.2 \text{ Hz} \), 4H, a-H), 8.69 (d, \( ^3J = 6.0 \text{ Hz} \), 4H, d-H), 8.70 (s, 2H, β-H), 8.75 (d, \( ^3J = 4.6 \text{ Hz} \), 2H, β-H), 8.86 (d, \( ^3J = 4.6 \text{ Hz} \), 2H, β-H), 8.89 (s, 2H, β-H) ppm. \( ^13C \text{ NMR (CDCl}_3, 100 \text{ MHz)}: \delta = 21.4, 21.7, 118.4, 118.9 \) (2C), 121.0, 125.4, 126.7, 127.8 (4C), 130.5 (4C), 132.9, 135.0,
135.5, 137.8, 138.1, 139.4, 142.7, 144.6, 150.3 ppm. **Elemental analysis:** Anal. Calcd for C₆₄H₅₂N₆: C, 84.92; H, 5.79; N, 9.28. Found: C, 84.69; H, 5.40; N, 9.18. **ESI-MS:** m/z (%) 905.5 (100) [M + H]^+.

Zinc porphyrin 1

**Compound 7** (50.0 mg, 55.2 μmol) was dissolved in 10 mL of CHCl₃. After addition of Zn(OAc)₂•2H₂O (121 mg, 552 μmol) in 5 mL of CH₃OH, the reaction mixture was allowed to stir at room temperature for 6 h. Then the solvent was evaporated and the concentrated crude passed through SiO₂ gel in THF to furnish the pure product 1 (53.0 mg, 95%). It is only partially soluble in THF due to O₃THF→ZnPor complexation, which breaks the axial Nₚy→ZnPor coordination. **Rf** = 0.4 (SiO₂, 4% MeOH in CH₂Cl₂). **mp:** > 200 ºC. **IR (KBr):** ν = 553, 721, 795, 995, 1064, 1203, 1336, 1414, 1480, 1595, 2853, 2917, 3023, 3434 cm⁻¹.

**¹H NMR (THF-δ₈, 400 MHz):** δ = 1.84 (s, 12H, f-H), 2.59 (s, 6H, g-H), 7.28 (s, 4H, e-H), 7.46 (d, ³J = 16.4 Hz, 2H, m-H), 7.54 (d, ³J = 6.0 Hz, 4H, c-H), 7.77 (d, ³J = 16.4 Hz, 2H, n-H), 7.99 (d, ³J = 8.2 Hz, 4H, b-H), 8.21 (d, ³J = 8.2 Hz, 4H, a-H), 8.47 (d, ³J = 6.0 Hz, 4H, d-H), 8.63 (s, 2H, β-H), 8.66 (d, ³J = 4.6 Hz, 2H, β-H), 8.82 (d, ³J = 4.6 Hz, 2H, β-H), 8.85 (s, 2H, β-H) ppm. **¹³C NMR (THF-δ₈, 100 MHz):** The low solubility of the compound does not allow recording the ¹³C NMR. **Elemental analysis:** Anal. Calcd for C₆₄H₅₀N₆Zn•0.1 CH₂Cl₂: C, 78.80; H, 5.18; N, 8.60. Found: C, 78.66; H, 5.03; N, 8.35. **ESI-MS:** m/z (%) 968.7 (100) [M + H]^+. 55
1.3 Synthesis and Characterization of Nanorotors

Pre-Rotor Complex PreROT-1:

For preparation, see main paper. Due to the formation of hetero-assembly and slow rotation of the aryl groups directly connected to the porphyrin rings, protons e-, e'-H and f-, f'-H experience different chemical environments. One set resides inside the sandwich and the other resides outside. In the complex, two sets of phenanthroline protons were observed in 1:1 ratio where one set refers to the HETPYP-I complexed phenanthroline stations denoted as c and the other set stands for uncomplexed phenanthroline stations assigned as u. After formation of the complex with the pyridine arm of the rotator, bond rotation of the duryl and mesityl groups ceases and as a consequence protons 12-H, 14-H and 15-H split into two sets in 1:1 ratio for complexed phenanthroline stations. Similarly protons 10-, 11-, a-, b-H are also split.

**1H NMR (CD$_2$Cl$_2$, 400 MHz):** $\delta = \{4.96-4.92\} (m, 6H, CH$_2$, DABCO), \{4.86-4.82\} (m, 6H, CH$_2$, DABCO), 1.45 (s, 6H, f-H), 1.52 (s, 6H, f'-H), 1.97 (s, CH$_3$, CH$_3$CN from [Cu(CH$_3$CN)$_4$]PF$_6$), 2.02 (s, 6H, 14c-H), 2.05 (s, 18H, 14c'-H + 14u-H), 2.09 (s, 12H, 12u-H), 2.15 (s, 6H, 12c-H), 2.17 (s, 6H, 12c'-H), 2.38 (s, 6H, 13u-H), 2.48 (s, 6H, 13c-H), 2.58 (s, 6H, 15c-H), 2.60 (s, 6H, g-H), 2.64 (s, 6H, 15c'-H), 2.74 (s, 12H, 15u-H), 6.62 (d, $^3J = 6.4$ Hz, 4H, d-H), 6.97 (d, $^3J = 8.0$ Hz, 2H, s-H), 7.01 (s, 4H, 9u-H), 7.12 (s, 2H, 9c-H), 7.15 (s, 2H, 9c'-H), 7.17 (s, 2H, e-H), 7.30 (s, 2H, e'-H), 7.36 (d, $^3J = 6.4$ Hz, 4H, c-H), 7.38 (d, $^3J =$
16.4 Hz, 2H, m-H), 7.47 (d, $^3J = 8.0$ Hz, 2H, s-H), 7.60 (d, $^3J = 8.2$ Hz, 2H, [8/3]u-H), 7.63 (d, $^3J = 8.2$ Hz, 2H, [3/8]u-H), 7.70 (d, $^3J = 8.0$ Hz, 2H, s-H), 7.80 (d, $^3J = 16.4$ Hz, 2H, n-H), 7.90 (d, $^3J = 8.0$ Hz, 2H, s-H), 7.91 (d, $^3J = 8.0$ Hz, 2H, s-H), 7.92 (d, $^3J = 8.0$ Hz, 2H, s-H), 7.96 (s, 4H, [5+6]-uH), 7.97 (d, $^3J = 8.0$ Hz, 2H, s-H), 7.99 (d, $^3J = 8.0$ Hz, 2H, s-H), 8.03 (d, $^3J = 8.2$ Hz, 4H, [3+8]c-H), 8.04 (d, $^3J = 8.0$ Hz, 2H, s-H), 8.08 (d, $^3J = 8.0$ Hz, 2H, s-H), 8.24 (s, 4H, [5+6]-cH), 8.27 (d, $^3J = 8.0$ Hz, 2H, s-H), 8.35 (s, 2H, β(1)-H), 8.38 (d, $^3J = 8.2$ Hz, 2H, [7/4]u-H), 8.41 (d, $^3J = 4.6$ Hz, 2H, β(1)-H), 8.42 (d, $^3J = 8.2$ Hz, 2H, [4/7]u-H), 8.49 (d, $^3J = 8.0$ Hz, 2H, s-H), 8.53 (d, $^3J = 4.6$ Hz, 2H, β(1)-H), 8.57 (s, 2H, β(1)-H), 8.61 (s, 2H, β(2)-H), 8.66 (d, $^3J = 4.6$ Hz, 2H, β(2)-H), 8.69 (d, $^3J = 4.6$ Hz, 2H, β(2)-H), 8.72 (s, 2H, β(2)-H), 8.78 (d, $^3J = 8.2$ Hz, 2H, [7/4]c-H), 8.79 (d, $^3J = 8.2$ Hz, 2H, [4/7]c-H) ppm.

**Elemental analysis:** Anal. Calcd for C_{246}H_{202}Cu_{12}N_{20}P_{2}Z_{2}•3CH_{2}Cl_{2}: C, 70.52; H, 4.94; N, 6.61. Found: C, 70.96; H, 4.54; N, 6.67. **ESI-MS:** m/z (%) 1792.1 (100) [Cu_{2}(1)(2)]^{2+}, 1844.6 (10) [Cu_{2}(1)(2)(DABCO)]^{2+}.

**Nanorotor ROT-1:**

For preparation, see main paper. **IR (KBr):** $\nu$ = 552, 632, 659, 721, 796, 827, 850, 995, 1038, 1064, 1108, 1203, 1336, 1382, 1417, 1480, 1522, 1596, 1632, 2236, 2852, 2916, 3025, 3436 cm$^{-1}$. **$^1$H NMR (CD$_2$Cl$_2$, 400 MHz):** $\delta = -[4.95-4.91]$ (m, 6H, CH$_2$, DABCO), $-[4.85-4.81]$ (m, 6H, CH$_2$, DABCO), 1.45 (s, 6H, f-H), 1.52 (s, 6H, f'-H), 1.98 (s, CH$_3$, CH$_3$CN from [Cu(CH$_3$CN)$_4$]PF$_6$), 2.02 (s, 6H, 14c-H), 2.05 (s, 18H, 14c'-H + 14Cu-H), 2.08 (s, 12H,
12Cu-H), 2.16 (s, 6H, 12c-H), 2.17 (s, 6H, 12c'-H), 2.40 (s, 6H, 13Cu-H), 2.48 (s, 6H, 13c-H), 2.57 (s, 6H, 15c-H), 2.60 (s, 6H, g-H), 2.64 (s, 6H, 15c'-H), 2.77 (s, 12H, 9Cu-H), 7.07 (s, 4H, 9Cu-H), 7.12 (s, 2H, 9c-H), 7.15 (s, 2H, 9c'-H), 7.18 (s, 2H, e-H), 7.28 (s, 2H, e'-H), 7.37 (d, ^3J = 6.2 Hz, 4H, c-H), 7.39 (d, ^3J = 16.4 Hz, 2H, m-H), 7.54 (d, ^3J = 8.0 Hz, 2H, s-H), 7.71 (d, ^3J = 8.0 Hz, 2H, s-H), 7.80 (d, ^3J = 16.4 Hz, 2H, n-H), 7.90 (d, ^3J = 8.0 Hz, 2H, s-H), 7.91 (d, ^3J = 8.0 Hz, 2H, s-H), 7.92 (d, ^3J = 8.0 Hz, 2H, s-H), 7.94 (d, ^3J = 8.2 Hz, 2H, [8/3]Cu-H), 7.98 (d, ^3J = 8.0 Hz, 2H, s-H), 8.00 (d, ^3J = 8.2 Hz, 2H, [8/3]c-H), 8.02 (d, ^3J = 8.2 Hz, 2H, [3/8]c-H), 8.03 (d, ^3J = 8.0 Hz, 2H, s-H), 8.04 (d, ^3J = 8.0 Hz, 2H, s-H), 8.18 (s, 2H, [5/6]Cu-H), 8.19 (s, 2H, [6/5]Cu-H), 8.24 (s, 4H, [5+6]-cH), 8.27 (d, ^3J = 8.0 Hz, 2H, s-H), 8.34 (s, 2H, β(1)-H), 8.40 (d, ^3J = 4.6 Hz, 2H, β(1)-H), 8.49 (d, ^3J = 8.0 Hz, 2H, s-H), 8.54 (d, ^3J = 4.6 Hz, 2H, β(1)-H), 8.58 (s, 2H, β(1)-H), 8.59 (s, 2H, β(2)-H), 8.65 (d, ^3J = 4.6 Hz, 2H, β(2)-H), 8.70 (d, ^3J = 8.2 Hz, 2H, [7/4]Cu-H), 8.71 (d, ^3J = 4.6 Hz, 2H, β(2)-H), 8.74 (s, 2H, β(2)-H), 8.75 (d, ^3J = 8.2 Hz, 2H, [4/7]Cu-H), 8.77 (d, ^3J = 8.2 Hz, 2H, [7/4]c-H), 8.78 (d, ^3J = 8.2 Hz, 2H, [4/7]c-H) ppm. ESI-MS: m/z (%) 927.2 (100) [Cu_{4}(1)(2)]^{4+}.

**Nanorotor ROT-1_{100}^{CD,CN}:**

**ROT-1_{100}^{CD,CN}** was prepared by evaporating CD_{2}Cl_{2} from ROT-1 and redissolving it in CD_{3}CN. Despite the change of solvent the assembly remains intact. In CD_{3}CN, the rotational frequency is much enhanced in comparison to CD_{2}Cl_{2}. Due to fast rotation in **ROT-1_{100}^{CD,CN}**, there is only a single set for all phenanthroline protons, while in ROT-1, two sets are visible.
in a 1:1 ratio. Due to fast rotation, the symmetry in ROT-1\textsubscript{100}\textsuperscript{CD,CN} is increased and protons \(\beta(2)\) appear as a singlet. In contrast, in ROT-1 protons \(\beta(2)\) appear as two singlets and two doublets. \(^1\text{H} \text{NMR (CD}_3\text{CN, 400 MHz):}\) \(\delta = -5.01\) (s, 6H, CH\textsubscript{2}, DABCO), \(-4.91\) (s, 6H, CH\textsubscript{2}, DABCO), 1.27 \(\) (s, 6H, f-H), 1.44 \(\) (s, 6H, f'-H), 1.92 \(\) (s, 24H, 14-H, covered with CHD\textsubscript{2}CN signal), 2.04 \(\) (s, 24H, 12-H), 2.35 \(\) (s, 12H, 13-H), 2.57 \(\) (s, 6H, g-H), 2.65 \(\) (bs, 24H, 15-H), 7.04 \(\) (s, 8H, 9-H), 7.27 \(\) (s, 4H, e-H), 7.47 \(\) (d, \(J = 6.4\) Hz, 4H, d-H), 7.50 \(\) (d, \(J = 16.0\) Hz, 2H, m-H), 7.56 \(\) (d, \(J = 6.4\) Hz, 4H, c-H), 7.89 \(\) (d, \(J = 16.0\) Hz, 2H, n-H), 7.92 \(\) (d, \(J = 8.2\) Hz, 8H, [3+8]-H), 8.00 \(\) (d, \(J = 8.0\) Hz, 16H, s-H), 8.25 \(\) (s, 8H, [5+6]-H), 8.26 \(\) (s, 2H, \(\beta(1)-\)H), 8.32 \(\) (d, \(J = 4.6\) Hz, 2H, \(\beta(1)-\)H), 8.51 \(\) (d, \(J = 4.6\) Hz, 2H, \(\beta(1)-\)H), 8.56 \(\) (s, 2H, \(\beta(1)-\)H), 8.63 \(\) (bs, 8H, \(\beta(2)-\)H), 8.80 \(\) (d, \(J = 8.2\) Hz, 8H, [4+7]-H) \(\) (8H for spacers s became very broad and almost lie in the baseline near 7.6 ppm).

**Nanorotor ROT-1\textsubscript{x}\textsuperscript{CD,CN}** (where \(x\) is the v/v % of CD\textsubscript{3}CN in CD\textsubscript{2}Cl\textsubscript{2}):

ROT-1\textsubscript{x}\textsuperscript{CD,CN} was prepared by evaporating the solvent CD\textsubscript{2}Cl\textsubscript{2} from freshly prepared ROT-1 and dissolving it again in \(x\) volume% of CD\textsubscript{3}CN in CD\textsubscript{2}Cl\textsubscript{2}.

**Reversible conversion between ROT-1 and ROT-1\textsubscript{x}\textsuperscript{CD,CN}**:

Reversible cycle between ROT-1 and ROT-1\textsubscript{x}\textsuperscript{CD,CN} can be performed several times just by removing the solvent and dissolving it again in proper solvent mixture.

**Nanorotor ROT-1\textsubscript{y}\textsuperscript{l–}**:

To ROT-1 \(y\) equiv of tetra-\(n\)-butylammonium iodide was added to furnish ROT-1\textsubscript{y}\textsuperscript{l–}.

**Reversible conversion between ROT-1 and ROT-1\textsubscript{y}\textsuperscript{l–}**:

Reversible preparations of ROT-1 and ROT-1\textsubscript{y}\textsuperscript{l–} can be performed several times just by addition of \(y\) equiv of tetra-\(n\)-butylammonium iodide and addition of \(y\) equiv of AgBF\textsubscript{4}, respectively.
2. NMR Spectra

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

**Figure S2.** $^{13}$C NMR of compound 7 in CDCl$_3$ (100 MHz, 298 K).
Figure S3. $^1$H NMR of compound 1 in THF-$d_8$ (400 MHz, 298 K).

Figure S4. $^1$H NMR (400 MHz, 298 K) of assembly Pre ROT-1 in CD$_2$Cl$_2$. Two sets of phenanthroline and mesityl (at phenanthroline)/duaryl protons are observed in 1:1 ratio; one for HETPYP-I complexed protons, denoted as c and other for unloaded station designated as u.
Figure S5. $^1$H-$^1$H COSY NMR of PreROT-1 in CD$_2$Cl$_2$ (400 MHz, 298 K). Two sets of phenanthroline and mesityl (at phenanthroline)/duryl protons are observed in 1:1 ratio; one for HETPYP-I complexed protons, represented as c and other for unloaded station denoted as u.

Figure S6. $^1$H NMR of ROT-1 in CD$_2$Cl$_2$ (400 MHz, 298 K). Cu$^+$-loaded and HETPYP-I complexed phenanthroline and mesityl (at phenanthroline)/duryl protons do not merge in one single set due to impeded rotation in ROT-1. They appear as two sets in 1:1 ratio; the Cu$^+$-loaded station is denoted as Cu and HETPYP-I complexed station is indicated as c.
Figure S7. $^1$H-$^1$H COSY NMR of ROT-1 in CD$_2$Cl$_2$ (400 MHz, 298 K). Cu$^+$-loaded and HETPYP-I complexed phenanthroline and mesityl (at phenanthroline)/ duryl protons do not merge in one single set due to impeded rotation in ROT-1. They appear as two sets in 1:1 ratio; the Cu$^+$-loaded station is denoted as Cu and HETPYP-I complexed station is symbolized as c.

Figure S8. $^1$H NMR comparison of PreROT-1 and ROT-1 in CD$_2$Cl$_2$ (400 MHz, 298 K). In both cases two sets of phenanthroline and mesityl (at phenanthroline)/ duryl protons are observed. Protons at HETPYP-I complexed stations are denoted as c, protons at unloaded stations are designated as u and those at Cu$^+$-loaded stations are indicated as Cu. Upon loading Cu$^+$ to uncomplexed phenanthroline the protons shift to downfield.
Figure S9. $^1$H NMR of assembly $\text{ROT-1}_{100}^{\text{CD}_3\text{CN}}$ in CD$_3$CN (400 MHz, 298 K). All phenanthroline protons emerge in one set due to fast rotation of rotor.

Figure S10. $^1$H-$^1$H COSY NMR of $\text{ROT-1}_{100}^{\text{CD}_3\text{CN}}$ in CD$_3$CN (400 MHz, 298 K). All phenanthroline protons emerge in one set due to fast rotation of rotor.
3. Titration of nanorotor ROT-1 with CD$_3$CN, Tetra-$n$-butyl ammonium iodide and Triphenylphosphine

Figure S11. $^1$H NMR (400 MHz, 298 K) comparison of ROT-1$_{100}^{CD_3CN}$, ROT-1$_{80}^{CD_3CN}$, ROT-1$_{75}^{CD_3CN}$, ROT-1$_{66}^{CD_3CN}$, ROT-1$_{50}^{CD_3CN}$ and ROT-1$_{33.3}^{CD_3CN}$, i.e. in 100%, 80%, 75%, 66%, 50% and 33.3% CD$_3$CN (in CD$_2$Cl$_2$), respectively.
Figure S12. $^1$H NMR (400 MHz, 298 K) comparison of ROT-1$_{33.3}^{CD_3CN}$, ROT-1$_{25}^{CD_3CN}$, ROT-1$_{20}^{CD_3CN}$, ROT-1$_{16.7}^{CD_3CN}$, ROT-1$_{18.3}^{CD_3CN}$, ROT-1$_{15.0}^{CD_3CN}$, ROT-1$_{13.3}^{CD_3CN}$ and ROT-1 in 33.3%, 25%, 20%, 16.7%, 8.3%, 5.0%, 3.3% and 0% CD$_3$CN (in CD$_2$Cl$_2$), respectively.
**Figure S13.** Partial experimental and simulated $^1$H NMR (400 MHz, 298 K) of ROT-1$_x^{CD, CN}$ shows splitting of 13-H in 13c- and 13Cu-H (1:1 ratio) with corresponding rotational rate and % of CD$_3$CN present in CD$_2$Cl$_2$.

**Figure S14.** Sigmoidal dependence of rotational frequency of ROT-1$_x^{CD, CN}$ on concentration of added CD$_3$CN to ROT-1.
Figure S15. $^1$H NMR (400 MHz, 298 K) comparison of ROT-1 in presence of different equivalents of iodide (ROT-1$_x$I$^-$) in CD$_2$Cl$_2$.

Note (added to a reviewer’s comment): When one analyzes the various split signals about the binding site we can identify several pairs 5c/5Cu, 9c/9Cu, 13c/13Cu, and 14c/14Cu where the signals merge. In contrast, the pair 12c/12Cu – as indicated by the reviewer – is not merging. How is this possible in light of rapid rotation? The explanation is straightforward. When the motion of the rotator is rapid, all four stations experience a pyridine→copper interaction that will restrict rotational degrees of freedom of both aryl groups at the phenanthroline. As a consequence one expects the ortho-methyl groups 12-H and 14-H to exhibit two signals each (e.g. 12-H and 12-H') even at high speed due to possible loss of rotation. In one case we see the splitting (14c/14Cu) disappear at faster motion, in the other not (12c/12Cu). Apparently, due to proximity of the rotator arm, the ortho proton set of 12c/12Cu is transformed in 12-H and 12-H'.
**Figure S16.** Partial experimental and simulated $^1$H NMR (400 MHz, 298 K) of ROT-1 and ROT-1$_{13}^{13}$ in CD$_2$Cl$_2$ shows the splitting of 13-H in 13c and 13Cu-H (1:1 ratio) with the corresponding rotational frequency and equiv of added iodide.
Figure S17. Sigmoidal dependence of rotational frequency of ROT-1, on equiv of added tetra-$n$-butyl ammonium iodide to ROT-1.
Figure S18. $^1$H NMR (400 MHz, 298 K) comparison of ROT-1 in presence of different equivalents of PPh$_3$ (ROT-1$_y$PPh$_3$) in CD$_2$Cl$_2$. Addition of PPh$_3$ to the system generates new sets of phenanthroline protons as it binds strongly to Cu$^+$ phenanthroline. Even after addition of excess of PPh$_3$ to the system, the Cu$^+$-loaded and HETPYP-I complexed phenanthroline did not merge in a single set. The signal by a red asterisk denotes proton 9-H of the Cu$^+$-loaded phenanthroline station which binds to PPh$_3$. 
Figure S19. $^1$H NMR (400 MHz, 298 K) comparison of ROT-1 and ROT-1$_6$PPh$_3$(ROT-1 + 6 eq PPh$_3$) in presence of different equivalents of TBAI (tetra-$n$-butyl ammonium iodide) in CD$_2$Cl$_2$. 
4. Variable Temperature $^1$H NMR Spectra

The kinetics of rotation was analyzed at various temperatures using the program WinDNMR6 for the simulation of the experimental $^1$H NMR spectra. The spectra simulation providing the rate constants was performed using the model of a 2-spin system that undergoes mutual exchange. Activation parameters were determined from an Eyring plot.

![Variable Temperature $^1$H NMR Spectra](image)

**Figure S20.** VT $^1$H NMR (600 MHz) of ROT-1$^{CD, CN}_{110}$ in CD$_3$CN shows the broadening of protons (5+6)-, 9-, 15/14-, 13-, 12-H and splitting of e-, f- and 14/15-H at different temperatures. Two DABCO peaks at negative shift throughout the temperature range prove the intactness of the assembly.

**Table S1.** Activation parameters for ROT-1$^{CD, CN}_{16,7}$ at 298 K obtained from Eyring plot.

| $\Delta G_{298}^{\ddagger}$ (kJ mol$^{-1}$) | $\Delta H_{298}^{\ddagger}$ (kJ mol$^{-1}$) | $\Delta S_{298}^{\ddagger}$ (J mol$^{-1}$ K$^{-1}$) |
|------------------------------------------|------------------------------------------|------------------------------------------|
| 50.6                                     | 53.8                                     | 10.5                                     |
Figure S21. VT $^1$H NMR (600 MHz) of ROT-116.7$_{16,7}^{CD, CN}$ in CD$_2$Cl$_2$:CD$_3$CN = 5:1 shows the splitting of protons (5+6)-; 9-; 15,14-; 13-; 12-; e- and f-H at different temperature. Two peaks at negative shift throughout the temperature range prove the intactness of the assembly.

Figure S22. (a) Partial experimental and simulated VT $^1$H NMR (600 MHz) of ROT-116.7$_{16,7}^{CD, CN}$ in CD$_2$Cl$_2$:CD$_3$CN = 5:1 shows the splitting of 9-H at different temperatures with corresponding rotational frequency. (b) Eyring plot for rotational dynamics of ROT-116.7$_{16,7}^{CD, CN}$.
5. $^1$H-$^1$H ROESY NMR Spectra

Figure S23. Partial $^1$H-$^1$H ROESY NMR (400 MHz, 298 K, mixing time = 300 ms) of ROT-1 in CD$_2$Cl$_2$. The blue correlation signals are for NOE and the red correlation signals are for exchange.
Figure S24. Partial $^1$H-$^1$H ROESY NMR (400 MHz, 298 K, mixing time = 300 ms) of ROT-1 in CD$_2$Cl$_2$ shows no exchange between HETPYP-I complexed phenanthroline protons (denoted as $c$) and Cu$^{2+}$-loaded phenanthroline protons (designated as Cu) in (a) aromatic region and (b) aliphatic region. None of the phenanthrolines and phenanthroline-substituted mesityl and duryl signals show exchange correlation. However there are exchange correlations for spacers (s-H) and for the porphyrin-substituted mesityl protons (e-H), which arise due to side rotation of phenyl and mesityl rings, directly connected to porphyrins. (c) Zoomed part of the ROESY spectrum exhibit the exchange between spacers s. Exchange rate was calculated using the formula $k = 1/[I_M(I_D/I_C + 1)]$, where $I_D$ = intensity of diagonal peak (2.11); $I_C$ = intensity of cross peak (1.00) and $t_M$ = mixing time (300 ms). The corresponding exchange rate was found to be $k = 1.1$ Hz.
Figure S25. Partial $^1$H-$^1$H ROESY NMR (400 MHz, 298 K, mixing time $= 300$ ms) of ROT-$I_{8,3}$CD$_3$CN in CD$_2$Cl$_2$:CD$_3$CN $= 11:1$. The blue correlation signals are for NOE and the red correlation signals are for exchange.
**Figure S26.** Partial $^1$H-$^1$H ROESY NMR (400 MHz, 298 K, mixing time = 300 ms) of ROT-1$_{8.3}$CD$_3$CN in CD$_2$Cl$_2$:CD$_3$CN = 11:1 shows exchange between HETPYP-I complexed phenanthroline protons (denoted as c) and Cu$^+$-loaded phenanthroline protons (designated as Cu) in (a) aromatic region and (b) aliphatic region. All of the phenanthroline and phenanthroline-substituted mesityl and duryl signals show exchange correlations. (c) Zoomed part of the ROESY spectrum exhibits the exchange between 12c- and 12Cu-H. Exchange rate was calculated using the formula $k = 1/[t_M (I_D/I_C + 1)]$, where $I_D$ = intensity of diagonal peak (1.34); $I_C$ = intensity of cross peak (1.00) and $t_M$ = mixing time (300 ms). The corresponding exchange rate was found to be $k = 1.4$ Hz.

**Figure S27.** Partial $^1$H-$^1$H ROESY NMR (400 MHz, 298 K, mixing time = 300 ms) of ROT-1$_{5.0}$CD$_3$CN in CD$_2$Cl$_2$:CD$_3$CN = 19:1. The blue color correlations are for NOE and the red color correlations are for exchange.
Figure S28. Partial $^1$H-$^1$H ROESY NMR (400 MHz, 298 K, mixing time = 300 ms) of ROT-15.0$_{CD_{3}CN}$ in CD$_2$Cl$_2$:CD$_3$CN = 19:1 shows the exchange between HETPYP-1 complexed phenanthroline protons (denoted as c) and Cu$^+$-loaded phenanthroline protons (indicated as Cu) in (a) aromatic and (b) aliphatic region. All of the phenanthroline and phenanthroline-substituted mesityl and duryl signals show exchange correlations. (c) Zoomed part of the ROESY spectrum exhibits the exchange between 12c- and 12Cu-H. Exchange rate was calculated using the formula $k = 1/[t_M(I_D/I_C + 1)]^4$, where $I_D$ = intensity of diagonal peak (3.34); $I_C$ = intensity of cross peak (1.71) and $t_M$ = mixing time (300 ms). Corresponding rate was found to be $k = 1.1$ Hz.
Figure S29. Partial $^1$H-$^1$H ROESY NMR (400 MHz, 298 K, mixing time = 300 ms) of ROT-1$_{33}$CD$_{3}$CN in CD$_2$Cl$_2$:CD$_3$CN = 29:1. The blue correlation signals are for NOE and the red correlation signals are for exchange.
Figure S30. Partial $^1$H-$^1$H ROESY NMR (400 MHz, 298 K, mixing time = 300 ms) of ROT-13$_{3,3}$CD$_3$CN in CD$_2$Cl$_2$:CD$_3$CN = 29:1 shows exchange between HETPYP-I complexed phenanthroline protons (indicated as c) and Cu$^{2+}$-loaded phenanthroline protons (denoted as Cu) in (a) aromatic and (b) aliphatic region. All of the phenanthroline and phenanthroline-substituted mesityl and duryl signals show exchange correlations. (c) Zoomed part of the ROESY spectrum shows the exchange between 12c- and 12Cu-H. Exchange rate was calculated using the formula $k = 1/[t_M(I_D/I_C + 1)]$, where $I_D$ = intensity of diagonal peak (3.51); $I_C$ = intensity of cross peak (1.00) and $t_M$ = mixing time (300 ms). The corresponding exchange occurs at $k = 0.7$ Hz.
6. DOSY NMR Spectra

The diffusion coefficient $D$ of ROT-1$_{16.7}^{CD,CN}$ was obtained from the DOSY spectrum and the corresponding hydrodynamic radius was calculated by using the Stokes-Einstein equation:

$$r = \frac{k_B T}{6 \pi \eta D}$$

Figure S31. $^1$H DOSY NMR of ROT-1$_{16.7}^{CD,CN}$ (600 MHz, 298 K) in CD$_2$Cl$_2$:CD$_3$CN = 6:1 showing a single diffusion coefficient $D = 3.2 \times 10^{-10}$ m$^2$ s$^{-1}$ (hydrodynamic radius $r = 17.0$ Å).
7. ESI-MS Spectra

Figure S32. ESI-MS of PreROT-1.

Figure S33. ESI-MS of ROT-1.
8. Measurement of Binding Constant

Determination of log $K$ for binding of PPh$_3$ to C1 by a UV-vis titration:

A solution of C1 (1.0 × 10$^{-5}$ M) was titrated with a 2.0 × 10$^{-4}$ M solution of PPh$_3$ in dichloromethane.

The full data (wavelength region: 200 - 400 nm) was analyzed using the SPECFIT/32 global analysis system (Spectrum Software Associates, Marlborough, MA). Result: log $K$ = 6.28 ± 0.40.

Figure S34. UV-vis titration of PPh$_3$ and C1.
9. References

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