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# Five-State Rotary Nanoswitch

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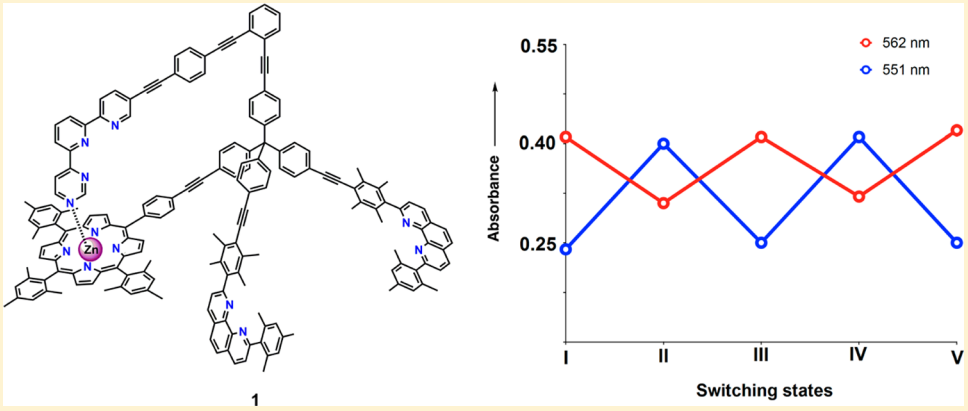
Supporting Information




**ABSTRACT:** In our quest to develop artificial multistate devices, we synthesized the nanomechanical switch **1** that is characterized by a tetrahedral core equipped with four pending arms. The rotary arm with its azaterpyridine terminal is intramolecularly coordinated to a zinc(II) porphyrin station that is the terminus of another arm in **1**. The two other arms carry identical sterically shielded phenanthroline stations. The 2-fold alternate addition of a copper(I) ion and [1,10]-phenanthroline (1 equiv each) results in the formation of five different switching states (State I→ State II→ State III→ State IV→ State V → State I), which force the toggling arm to move back and forth between the zinc(II) porphyrin and phenanthroline stations separated by a distance of 25 Å. All switching states constitute clean single species, except for State III, and thus are fully characterized by spectroscopic methods and elemental analysis. Finally, the initial state of nanoswitch was reset by addition of cyclam for complete removal of the copper(I) ions.

## INTRODUCTION

Among the most fascinating natural machineries,[1] the proton-powered rotary machine ATPase stands out due to its ability to synthesize adenosine triphosphate (ATP), the central "energy bar" in living organisms.[2] In a fascinating multistep mechanism, ATPase combines nanomechanical rotation with the sophisticated regulation of a chemical reaction. Inspired by nanomechanical action in nature,[3] a variety of stimuli-responsive artificial nanomachines[4,5] often based on rotaxane- and catenane-type architectures[6] have been developed, mainly over the past two decades: rotors,[7] switches,[8] shuttles,[9] muscles,[10] gears,[11] elevators,[12] walkers,[13] etc.[14] Some of these devices furthermore command the course of catalytic reaction(s),[15,16] cargo shipping,[17] and targeted drug release.[18]

The operation of any machine requires two, three, or more switching states.[19] For instance, the fascinating unidirectional motors, as designed by Feringa,[20] Lehn,[21] and others,[22] operate along a series of four rotary states requiring heat and light as alternate input. In nature, though, basically all machineries are based on chemical inputs, because chemical signaling and fuel(s) are available, while light energy is not.[23] This insight has triggered recent spectacular works on chemically fueled motors and devices, independently performed by Leigh,[23] Feringa,[24] and Nitschke.[25]

Herein, we report the design, synthesis and five-state switching of the three-station nanoswitch **1** applying external chemical stimuli. In recent years we have developed a family of triangular nanoswitches[15] that are alternatives to rotaxane and catenane-based systems[26] for rapid allosteric switching. Toggling in triangular nanoswitches has been used for commanding single-step,[15a−c,16] dual alternate,[15d] and two-step sequential[27] catalytic processes in an on/off manner, often over several switching cycles.

Nanoswitch **1** contains an azaterpyridine switching arm, one zinc(II) porphyrin station, and two enantiotopic phenanthroline stations. Based on previous findings concerning a two-station nanoswitch,[15c] in which an intramolecular copper(I) complex was replaced by an intermolecular copper(I) complex upon addition of 2-ferrocenyl-[1,10]-phenanthroline, we hypothesized that altogether five switching states may be possible in nanoswitch **1** with its three stations. We expected that alternate addition of copper(I) ions and [1,10]-phenanthroline (**2**) would toggle the rotary arm in **1** between the zinc(II) porphyrin and phenanthroline stations generating five different states (State I→ State II→ State III→ State IV→ State V). Finally, removal of all copper(I) ions should reset the original locked State I.

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## RESULTS AND DISCUSSION

**Design and Retrosynthetic Analysis.** To offer an additional station for the toggling arm, we moved away from our σ-symmetric nanoswitches[15] to a more versatile design based on the tetrahedral skeleton (Figure 1).[27] In the present work, we focus on a molecule with a rotary arm and three stations, two of which are identical, though. By considering our target, i.e. nanoswitch **1**, we selected the retrosynthetic strategy via **4** as displayed in Scheme 1, as it will allow the synthesis of a nanoswitch with three different stations in the future.

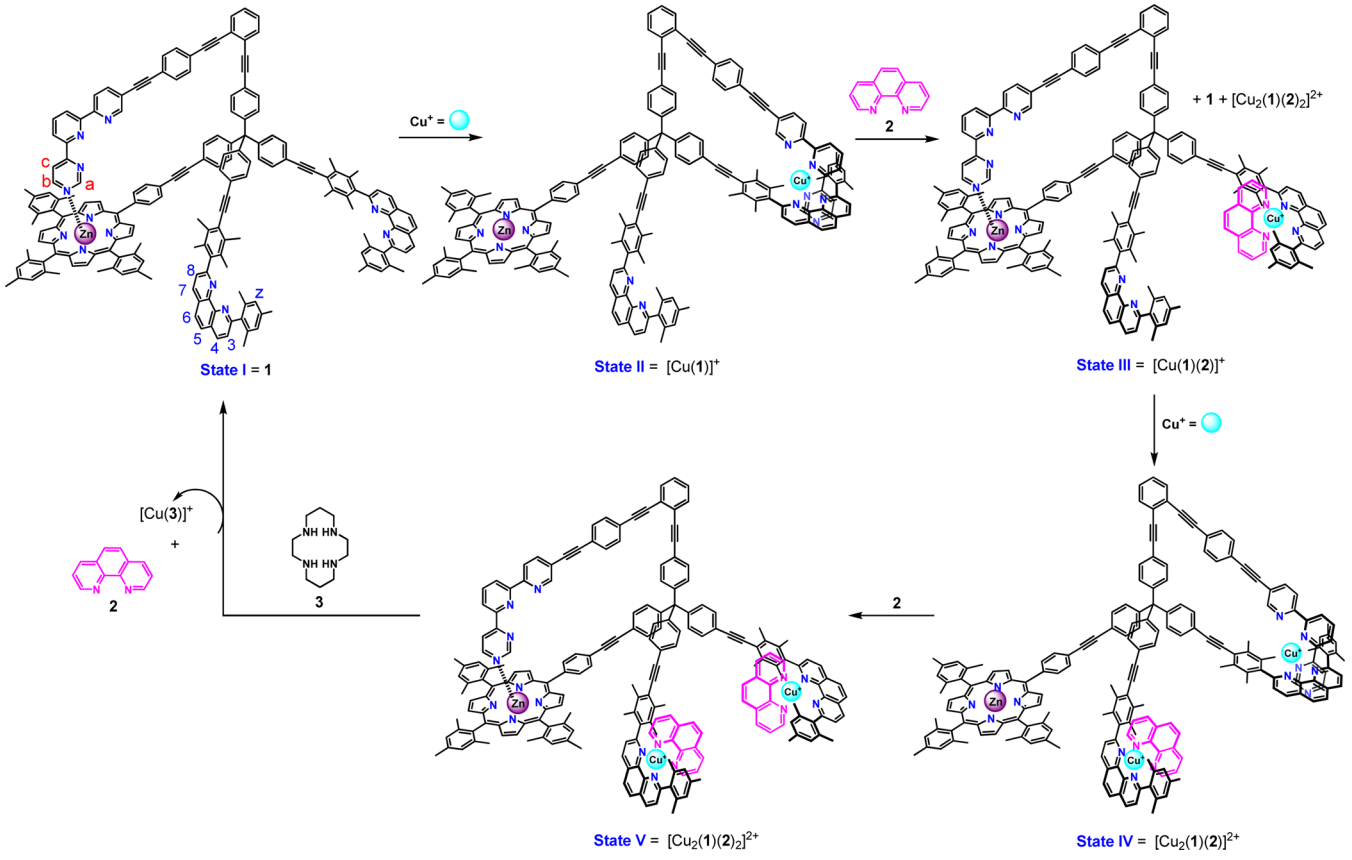
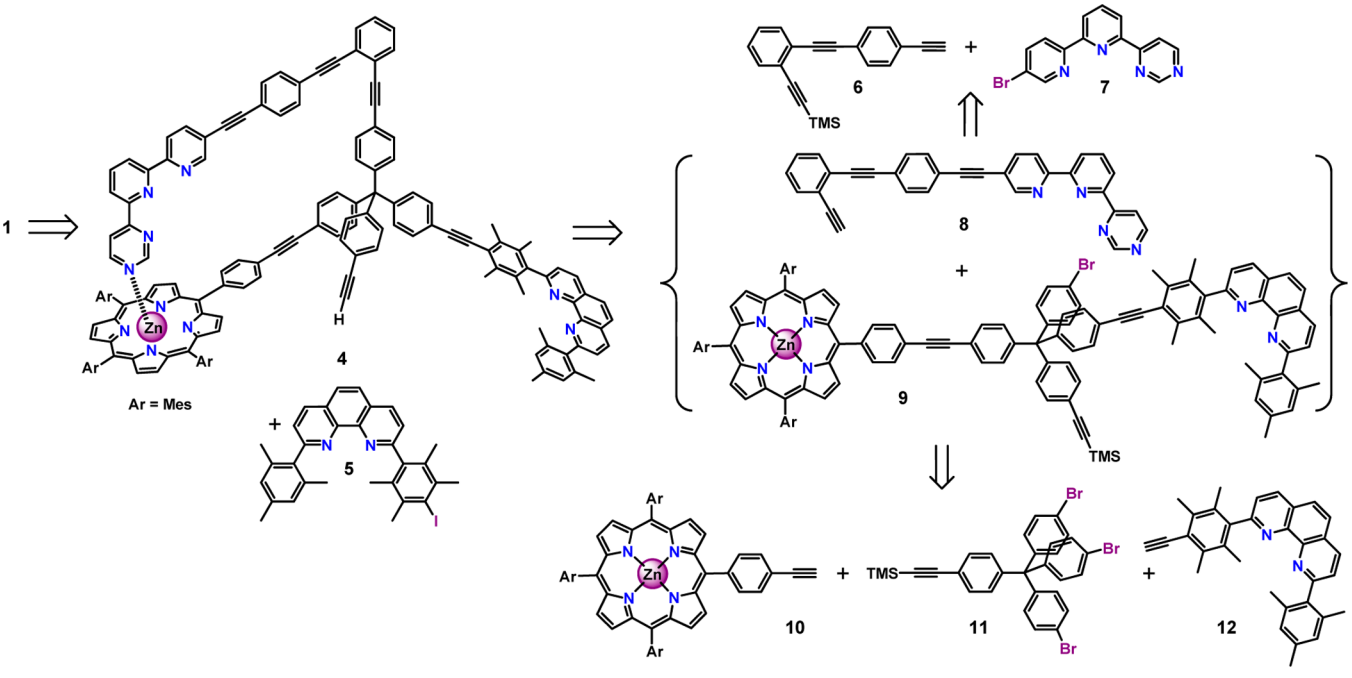



**Figure 1.** Schematic representation of the stimuli induced five-state switching.

**Scheme 1. Retrosynthetic Analysis of Rotary Switch 1**



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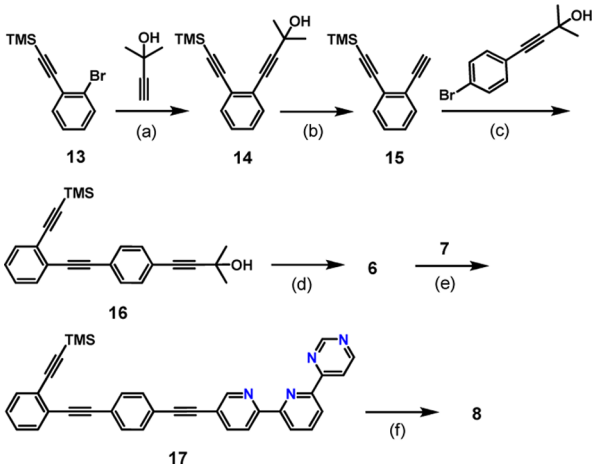
Switch **1** should be accessible by a cross-coupling of the two-state nanoswitch **4** with phenanthroline **5** in the presence of Pd(0) as a catalyst. To achieve the multistep synthesis of **4** with its three different arms, a convergent approach with high yields in each step is necessary. For instance, we decided to attach the rotary arm **8** in the second last step by considering its lengthy synthesis. Rotary arm **8** was expected to be accessible by a Sonogashira coupling of the terminal alkyne **6** and bromo-azaterpyridine **7**. The final preparation of **4** should then be possible in two steps by coupling of the tetraphenylmethane derivative **9** and rotary arm **8** followed by deprotection of the trimethylsilyl group. For compound **9**, we chose to attach the zinc(II) porphyrin and shielded phenanthroline group in a stepwise manner at the core unit **11**, the latter being prepared from tetra-(4-bromophenyl)methane. In all coupling steps, the formation of undesired di-, tri-, or tetra-coupled side products should be reduced by applying an excess of suitable starting material(s).

**Synthesis.** Rotary switch **1** was prepared through a multistep procedure along the retrosynthetic analysis shown in Scheme 1. The rotary arm **8** was afforded in six steps as outlined in Scheme 2.

**Scheme 2. Synthesis of Rotary Arm 8**[a]

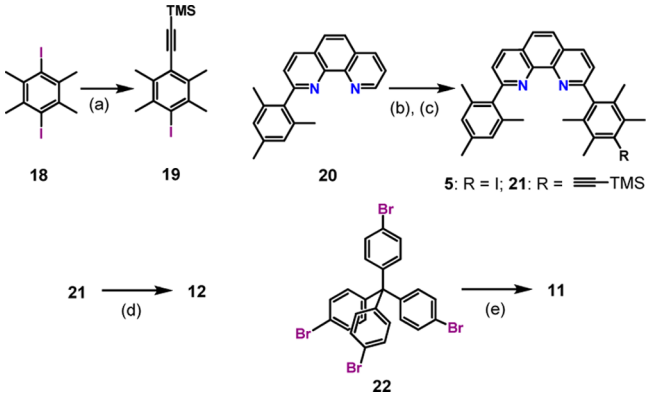



[a](a) $Pd(PPh_3)_4$, $Et_3N$, 80 °C, 48 h, 90%; (b) NaOH, PhMe, 130 °C, 30 min, 80%; (c) $Pd(PPh_3)_4$, $Et_3N$, 80 °C, 50 h, 74%; (d) NaOH, PhMe, 130 °C, 60 min, 92%; (e) $Pd(PPh_3)_4$, THF–$Et_3N$, 80 °C, 18 h, 86%; (f) aq. KOH, THF–MeOH, rt, 18 h, 85%.

First, Sonogashira coupling between ((2-bromophenyl)ethynyl)-trimethylsilane (**13**)[28] and 2-methylbut-3-yn-2-ol was followed by elimination of acetone from the resulting tertiary alcohol **14** in the presence of NaOH under vigorous reflux conditions to provide diyne **15**[29] in good yield. Thereafter, treatment of **15** with 4-(4-bromophenyl)-2-methylbut-3-yn-2-ol[30] under standard Sonogashira coupling conditions furnished compound **16** in 74% yield. After selective elimination of acetone from **16**, alkyne **6** was reacted with 5-bromo-6′-(pyrimidin-4-yl)-2,2′-bipyridine (**7**)[31] in the presence of Pd(0) to afford compound **17**. The latter was deprotected under aqueous basic conditions to yield the rotary arm **8** in 37% yield (over six steps).

The synthesis of phenanthroline derivatives **5** and **12** is depicted in Scheme 3. Compound **19** was prepared by a Sonogashira cross-coupling of **18**[32] with trimethylsilylacetylene (TMSA) at room temperature. Nucleophilic addition of monolithiated species obtained from both compounds **18**[32] and **19** to 2-mesityl-[1,10]-phenanthroline **20**[33] followed by subsequent oxidation

**Scheme 3. Synthesis of Phenanthroline Stations 5, 12, and Tetraphenyl Scaffold 11**[a]




[a](a) TMSA, $PdCl_2(PPh_3)_2$, CuI, $Et_3N$, rt, 3 h, 23–32%; (b) **18** or **19**, *n*-BuLi, (c) $MnO_2$, DCM, 55% (**5**), 61% (**21**); (d) aq. KOH, MeOH–THF, rt, 17 h, 94%; (e) TMSA, $Pd(PPh_3)_4$, CuI, $C_6H_6$–$Et_3N$, 55 °C, 18 h, 52%.

with $MnO_2$ furnished compounds **5**[7d] and **21**,[7d] respectively. The treatment of **21** with aqueous KOH in THF and MeOH afforded phenanthroline **12**.[7d]

Finally, the synthesis of rotary switch **1** via its precursors **25** and **4** was accomplished (Scheme 4). By using 4 mol % of $Pd(PPh_3)_4$, 1.70 equiv of trimethylsilylacetylene (TMSA), and a longer reaction time (17–18 h), compound **11**[34] was synthesized from tetrakis(4-bromophenyl)methane (**22**)[35] in improved yield (Scheme 3). Starting from **11**, switch **1** was afforded in five steps by utilizing multiple Sonogashira cross-coupling reactions. When an excess amount of **11** (3.0 equiv) was reacted with zinc(II) 5-(4-ethynylphenyl)-10,15,20-trimesitylporphyrin (**23**)[36] in triethylamine and DMF at 80 °C, the monocoupled porphyrin **24** was produced in 97% yield. A slight excess of **24** (2.0 equiv) was then reacted with phenanthroline **12** in a Pd(0) catalyzed Sonogashira transformation furnishing **9** in 76% yield. The latter was further coupled to the rotary arm **8** in the presence of $Pd(PPh_3)_4$ and cocatalyst $^tBu_3PHBF_4$[37] in $Et_3N$ and DMF affording nanoswitch **25** in 45% yield. Deprotection of compound **25** by treatment with aq. KOH solution in a THF–MeOH mixture yielded **4**, which was finally coupled with excess phenanthroline **5** to furnish the desired nanoswitch **1** in 52% yield.

Nanoswitch **1** (= State I) was fully characterized by NMR, UV/vis spectroscopy, ESI–MS, and elemental analysis. The ESI–MS spectrum of **1** displays a molecular ion peak at $m/z$ = 1255.4 Da for $[\mathbf{1} + 2H]^{2+}$, an assignment that is confirmed by the good agreement of the experimental and computed isotopic splitting pattern (Figure S57, Supporting Information (SI)). In the $^1H$ NMR, the pyrimidine protons a-H, b-H, and c-H of the azaterpyridine moiety appear highfield as sharp signals at 3.74, 2.70, and 6.84 ppm, respectively, confirming that the pyrimidyl ring is immersed into the ring currents of the zinc(II) porphyrin (ZnPor) (Figure S36, SI). In contrast, azaterpyridine derivative **17** shows the pyrimidyl protons a-H, b-H, and c-H at 9.33, 8.59, and 8.93 ppm, respectively (Figure S40, SI). Furthermore, the chemical shifts of a-H, b-H, and c-H protons in **1** are independent of the concentration ($c$ = 1.1 mM to 5.9 mM in DCM), which clearly suggests intramolecular coordination between the azaterpyridine rotary arm and ZnPor unit (Figure S41, SI). This conclusion was further supported by UV–visible spectroscopy: the Soret band absorption of **1** appears at 429 nm, whereas the uncoordinated zinc(II) porphyrin **24** shows its Soret absorption



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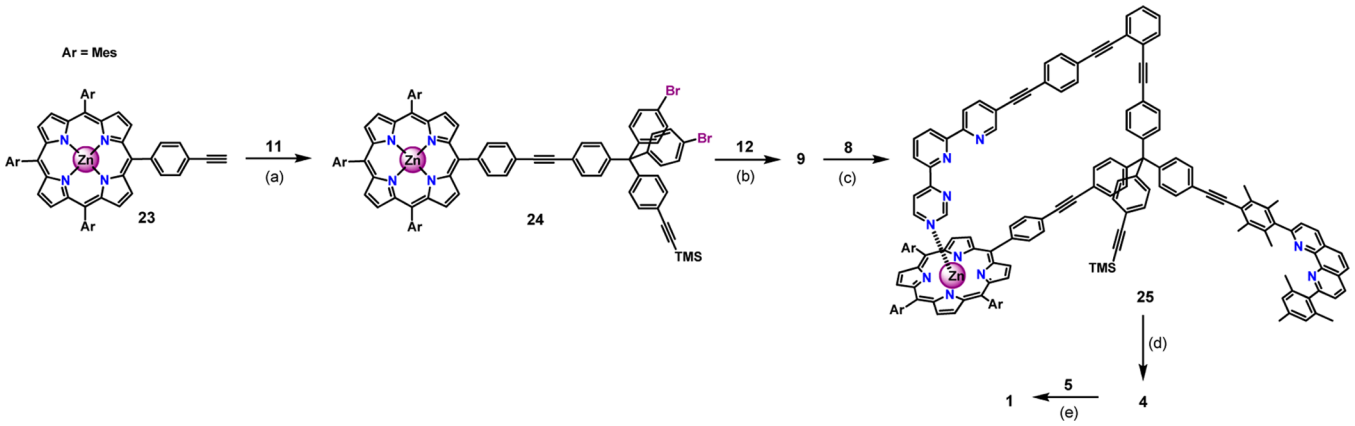
**Scheme 4. Synthesis of Rotary Switch 1**[a]




[a](a) $Pd(PPh_3)_4$, DMF–$Et_3N$, 80 °C, 36 h, 97%; (b) $Pd(PPh_3)_4$, DMF–$Et_3N$, 80 °C, 36 h, 76%; (c) $Pd(PPh_3)_4$, $^tBu_3PHBF_4$, DMF–$Et_3N$, 80 °C, 50 h, 45%; (d) aq. KOH, MeOH–THF, rt, 24 h, 96%; (e) $Pd(PPh_3)_4$, DMF–$Et_3N$, 60 °C, 24 h, 52%.

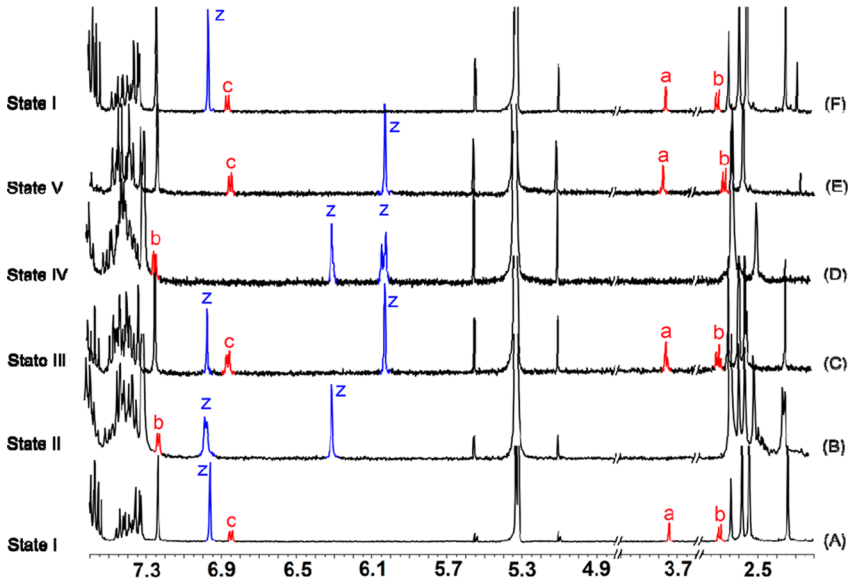



**Figure 2.** Partial $^1H$ NMR Spectra (400 MHz, $CD_2Cl_2$, 298 K): Five state switching from state I to state V: (A) **1** = State I; (B) after addition of 1.0 equiv of $Cu^+$ to state I affording state II = $[Cu(\mathbf{1})]^+$; (C) after addition of 1.0 equiv of [1,10]-phenanthroline 2 to state II yielding state III; (D) after addition of 1.0 equiv of $Cu^+$ to state III furnishing state IV = $[Cu_2(\mathbf{1})(\mathbf{2})]^{2+}$; (E) after addition of 1.0 equiv of [1,10]-phenanthroline to state IV yielding state V = $[Cu_2(\mathbf{1})(\mathbf{2})_2]^{2+}$; and (F) after addition of 2.0 equiv of cyclam resulting in regeneration of state I.

at 421 nm (Figure S62, SI). This 8 nm bathochromic shift is well-known from pyridine → zinc(II) porphyrin complexes.[15a] Intermolecular coordination was excluded by the concentration-independent Q-band absorption at 562 nm: the maximum remained constant when the concentration of **1** was varied from $c = 10^{-6}$ to $10^{-4}$ M (Figure S63, SI). In summary, these data demonstrate that rotary switch **1** is self-locked at the azaterpyridine → ZnPor binding.

**Addressing Five Different States of Rotary Nanoswitch 1.** At the onset, each switching state except State III was individually synthesized in pure form and characterized by $^1H$, $^1H$–$^1H$ COSY, UV/vis, ESI–MS, and elemental analysis (for procedures and data, see Experimental Section and SI). Thereafter, we investigated the formation of all five states of switching (State I→ State II→ State III→ State IV→ State V → State I) by alternate addition of $[Cu(MeCN)_4]^+$ and [1,10]-phenanthroline (Figure 2). The distinctive changes in $^1H$ NMR and UV/vis spectroscopic studies during the course of the five-state switching are shown in Figures 2 and 3 respectively. Addition of 1.0 equiv of $[Cu(CH_3CN)_4]B(C_6F_5)_4$ to a solution of switch **1** in $[D_2]$-dichloromethane yielded quantitatively the intramolecular heteroleptic HETTAP complex (HETeroleptic Terpyridine And Phenanthroline)[38] $[Cu(\mathbf{1})]^+$ (= State II). In $[Cu(\mathbf{1})]^+$ the azaterpyridine unit is connected via copper complexation to one of the two shielded phenanthroline stations. As a result, the azaterpyridine arm had to relocate from the zinc(II) porphyrin to the copper(I) binding site, i.e. a distance of 25 Å (molecular modeling). The assignment was supported by $^1H$, $^1H$–$^1H$ COSY, ESI–MS, elemental analysis, and UV–vis studies. In the NMR spectrum of $[Cu(\mathbf{1})]^+$, (i) protons a-H, b-H, and c-H of the azaterpyridine arm are shifted from 3.74, 2.70, and 6.84 ppm to the aromatic region (7.40, 7.23, and 7.61 ppm, respectively), and (ii) at the same time, the z-H protons of one phenanthroline station are upfield shifted from 6.96 to 6.30 ppm as a result of HETTAP complexation leaving the second phenanthroline station untouched (Figure S42, SI). The ESI–MS



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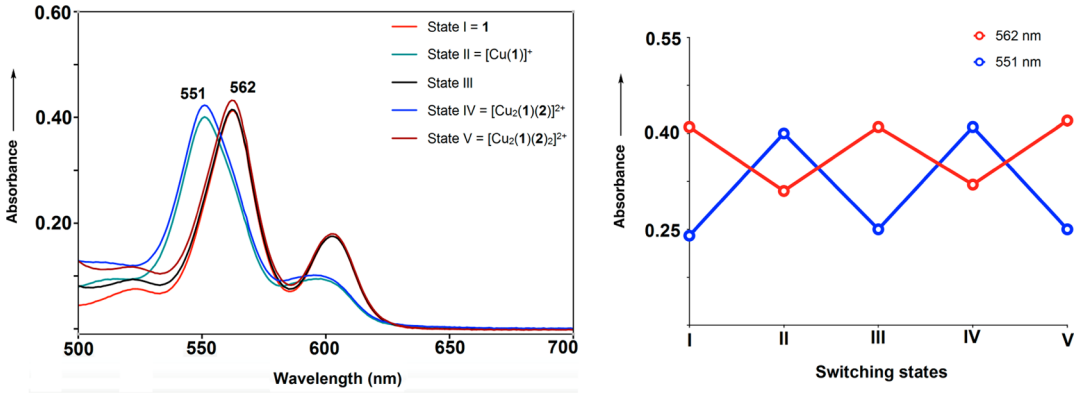


**Figure 3.** UV−vis spectral changes upon alternate addition of $Cu^{+}$ ions and [1,10]-phenanthroline to a solution of nanoswitch **1** (left). Absorbance changes at $\lambda$ = 562 nm (red trace) and at $\lambda$ = 551 nm (blue trace) from the same experiment (right).

**Table 1. Data of Switching States I to V**

| | shielded phenanthroline[a] station | | | | | | azaterpyridine arm[a] | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| state | z-H | 3-H | 4-H | 5,6-H | 7-H | 8-H | a-H | b-H | c-H | UV/vis/nm[b] |
| I | 6.96 | 7.58 | 8.36 | 7.91 | 8.34 | 7.54 | 3.74 | 2.70 | 6.84 | 429/562 |
| II | 6.30, 6.97 | 7.90 | 8.71 | 7.91, 7.93 | 8.46 | 7.70 | 7.40 | 7.23 | 7.61 | −/551 |
| III | − | − | − | − | − | − | − | − | − | −/562 |
| IV | 6.29, | 7.83− | 8.68− | 7.86, | 8.47− | 7.69− | 7.45 | 7.24 | 7.79 | −/551 |
| | 6.02 | 7.85 | 8.69 | 7.87 | 8.49 | 7.72 | | | | |
| V | 6.02 | 7.88 | 8.70 | 7.86 | 8.67 | 7.84 | 3.74 | 2.68 | 6.85 | −/562 |

[a]NMR shifts in ppm. [b]Absorption maxima.

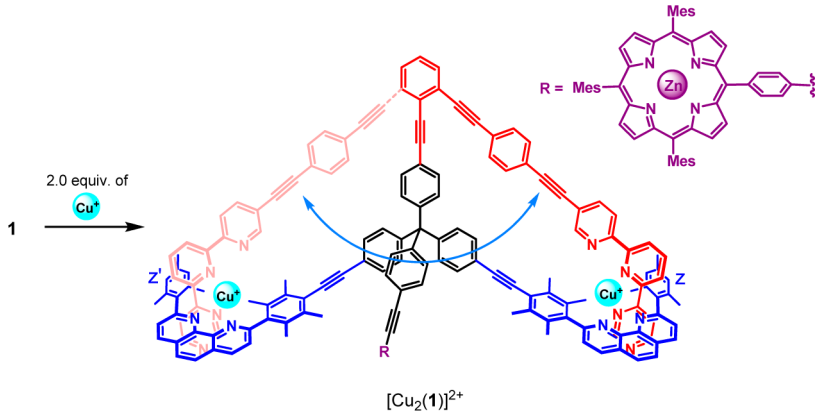


**Figure 4.** Schematic representation of oscillatory motion of azaterpyridine rotary arm between two phenanthroline stations in nanoswitch $[Cu_2(\mathbf{1})]^{2+}$.

exhibits a peak at 2623.4 Da that corresponds to the desired complex $[Cu(\mathbf{1})(MeOH)(H_2O)]^{+}$ (Figure S58, SI). Formation of the copper(I) complex is furthermore confirmed by its UV/vis spectrum, which shows a Q-band absorption at $\lambda$ = 551 nm that is typical for a noncoordinated zinc(II) porphyrin system (Figure S64, SI). Upon addition of 1.0 equiv of [1,10]-phenanthroline (**2**) to $[Cu(\mathbf{1})]^{+}$, the Q-band shifts back to 562 nm (Figure 3). However, State III is not a single species represented by $[Cu(\mathbf{1})(\mathbf{2})]^{+}$ (Figure S44, SI). Rather the $[Cu(\mathbf{2})]^{+}$ subunit self-sorts on both phenanthroline stations of **1** without preference, because complex formation at one arm does not influence the second arm decisively. As a result, a 1:1:1 mixture of **1**, $[Cu(\mathbf{1})(\mathbf{2})]^{+}$, and $[Cu_2(\mathbf{1})(\mathbf{2})_2]^{2+}$ was received as determined by integration and comparison of chemical shifts of the b-H proton.

Upon addition of 1.0 equiv of copper(I) ions to State III, the azaterpyridine arm detaches from the zinc(II) porphyrin station and moves to one of the two shielded phenanthroline stations thus cleanly affording the intramolecular complex $[Cu_2(\mathbf{1})(\mathbf{2})]^{2+}$ (= State IV). The $^{1}$H NMR was instructive in various ways: (i) the diagnostic downfield shift of pyrimidyl protons a-H and b-H to 7.45 and 7.24 ppm from their original position at ∼3.74 and ∼2.70 ppm, respectively, reveals an intramolecular HETTAP complexation with the shielded phenanthroline station, and (ii) simultaneously the z-H protons of the phenanthroline disappear at 6.96 and reappear at 6.29 ppm, which is equally indicative of an intramolecular HETTAP[38] complex in $[Cu_2(\mathbf{1})(\mathbf{2})]^{2+}$ (Figure S45, SI). The toggling of the arm is also visible from the color change from greenish violet to orange red. The ESI−MS analysis of the resultant complex shows a molecular ion peak at $m/z$ = 1407.9 (Figure S59, SI), which corroborates the formation of $[Cu_2(\mathbf{1})(\mathbf{2})]^{2+}$. The experimental splitting pattern is identical with the expected theoretical splitting pattern. When 1.0 equiv of [1,10]-phenanthroline was added to State IV, protons a-H and b-H of the pyrimidyl unit shifted to 3.74 and



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2.68 ppm, respectively. At the same time, all mesityl protons z-H of both phenanthroline stations appear as a singlet at 6.02 ppm, showing that both have the same chemical environment (Figure S46, SI). The ESI−MS spectrum corroborates State V, as only a single peak is detected at $m/z$ = 1498.9 Da suggesting formation of $[Cu_2(\mathbf{1})(\mathbf{2})_2]^{2+}$ (Figure S60, SI). Some of the characteristic signals when changing the switching states I → II → III → IV → V are shown in Table 1. Finally, 2 equiv of cyclam were added to remove copper(I) ions, which regenerated the initial locked State I, thus confirming a full reset of the nanoswitch **1** after five-state toggling (Figure 2). A UV−vis investigation showed that all switching events along States I → II, II → III, III → IV, and IV → V were instantaneous within mixing (less than 10 s).

Nanoswitch $[Cu_2(\mathbf{1})]^{2+}$ offers the chance to investigate the kinetics of a spontaneous toggling motion of the azaterpyridine arm between two copper(I)-loaded phenanthroline stations (Figure 4). We recorded variable temperature $^1$H NMR spectra in 1,1,2,2-tetrachloroethane-$D_2$. No coalescence of the z-H protons of the HETTAP complex at 6.28 ppm and z′-H protons of the frustrated copper(I)-loaded pheananthroline station at 7.00 ppm was observed by variable temperature $^1$H NMR studies at 298−373 K. Notably, attempts to trigger spontaneous toggling by adding coordinating ligands such as acetonitrile-$D_3$ and 4-iodopyridine were unsuccessful.

## CONCLUSION

In conclusion, we have described the design and synthesis of a rotary switch that has three stations to welcome the switching arm. The multistep synthesis is comprised of 13 new steps. Upon the alternate addition of copper(I) ion and the parent [1,10]-phenanthroline, the rotary switch undergoes a five-state switching event in which the arm is switched back and forth between the zinc(II) porphyrin and two copper(I)-loaded phenanthroline stations. Thus, we have successfully demonstrated multistate switching, which is an important step in the development of multiresponsive molecular nanomachinery.

## EXPERIMENTAL SECTION

**General Information.** All reagents were obtained from commercial suppliers and used without further purifications. Technical grade solvents were distilled before use. Tetrahydrofuran (THF) was predried over basic alumina and then distilled over potassium. Dimethylformamide (DMF) and triethylamine ($Et_3N$) were distilled on calcium hydride. Diethyl ether ($Et_2O$) was predried over calcium hydride and then distilled over sodium. The melting points of compounds are reported without correction. $^1$H, $^{13}$C, and $^1$H−$^1$H COSY NMR spectra were recorded at 298 K using the deuterated solvent as the lock. The chemical shifts refer to the residual protiated fraction of the solvent ($CHCl_3$: $\delta_H$ = 7.26 ppm, $\delta_C$ = 77.0 ppm; $CHDCl_2$: $\delta_H$ = 5.32 ppm, $\delta_C$ = 53.8 ppm). Abbreviations were used in $^1$H NMR assignments to describe splitting patterns (s: singlet, d: doublet, t: triplet, dd: doublet of doublet, ddd: doublet of doublet of doublet, bs: broad singlet, td: triplet of doublets, m: multiplet), the value of coupling constant(s) is reported in hertz (Hz), the number of protons are implied, and the assignments of protons are reported wherever possible. The numbering of carbon atoms is not in accordance with IUPAC nomenclature guidelines. All moisture- and air-sensitive reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Column chromatographic purifications were performed on silica gel 60 (60−230 mesh) or on neutral alumina (0.05−0.15 mm, Brockmann Activity 1). Thin Layer Chromatography (TLC) was performed using Merck silica gel (60 F254) or on neutral $Al_2O_3$ (150 F254) sheets. Size exclusion chromatography was performed on BioRads Biobeads-SX3 using toluene as an eluent. Compounds **5**,[7d] **11**,[34] and **12**[7d] were synthesized according to known literature procedures and in some cases with optimized conditions for improving yields (see Supporting Information). Compounds **15**[29] and **21**[7d] were prepared by a different route (Schemes 2 and 3, respectively), and their spectral data were in agreement with literature data.

*Synthesis of Compound* ***14***. To a mixture of compound **13**[28] (5.00 g, 19.8 mmol) and CuI (188 mg, 987 μmol) in anhydrous $Et_3N$ (150 mL) was added 2-methylbut-3-yn-2-ol (19.2 mL, 198 mmol), and the resultant mixture was flushed with $N_2$ for 45 min. $Pd(PPh_3)_4$ (1.14 g, 987 μmol) was added and the reaction mixture was heated to 80 °C for 48 h (TLC). The solvent was removed by rotary evaporation. The residue was dissolved in DCM (150 mL) and successively washed with deionized water (150 mL × 3) and saturated brine solution (150 mL). The organic layer was removed, dried over anhydrous $Na_2SO_4$, and evaporated in *vacuo*. The dark brown residue was purified by column chromatography on silica gel using 10% EtOAc in *n*-hexane ($R_f$ = 0.44, $SiO_2$, 30% EtOAc in *n*-hexane) to furnish **14** as viscous brown oil (4.60 g, 18.5 mmol, 90%). IR (neat): $\nu$ 3579, 3446, 3056, 2977, 2220, 2149, 1935, 1835, 1682, 1644, 1597, 1505, 1368, 1248, 1152, 1032, 958, 869, 757, 697, 642, 561, 502 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.46 (ddd, $^3J$ = 7.2 Hz, $^4J$ = 2.0 Hz, $^5J$ = 0.4 Hz, 1H), 7.40 (ddd, $^3J$ = 7.2 Hz, $^4J$ = 2.0 Hz, $^5J$ = 0.4 Hz, 1H), 7.22−7.24 (m, 2H), 2.16 (bs, 1H), 1.64 (s, 6H), 0.27 (s, 9H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 132.3, 131.8, 128.1, 127.9, 125.6, 125.3, 103.3, 98.1, 97.7, 80.8, 65.7, 31.5, 0.0 ppm.

*Synthesis of Compound* ***16***. A 250 mL was charged with compound **15** (1.50 g, 7.56 mmol), 4-(4-bromophenyl)-2-methylbut-3-yn-2-ol (1.44 g, 6.05 mmol), and CuI (72.0 mg, 378 μmol). Freshly distilled anhydrous $Et_3N$ (65 mL) was added, and the solution was sparged with $N_2$ for 40 min. After addition of $Pd(PPh_3)_4$ (436 mg, 377 μmol) the reaction mixture was heated to 80 °C for 50 h (TLC). The reaction was allowed to cool to room temperature, and the solvent was removed by rotary evaporation. The residue was dissolved in DCM (50 mL) and successively washed with deionized water (50 mL × 3) and a saturated brine (50 mL) solution. The organic layer was removed, dried over anhydrous $Na_2SO_4$, and evaporated. The chromatographic purification of crude product on silica gel using 10% EtOAc in *n*-hexane ($SiO_2$, $R_f$ = 0.50, EtOAc in *n*-hexane) furnished **16** as yellow solid (2.10 g, 5.89 mmol, 74%). Mp: 60−62 °C. IR (KBr): $\nu$ 3451, 3056, 2971, 2148, 1935, 1505, 1439, 1368, 1247, 1155, 1009, 958, 842, 759, 642, 561, 504 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.47−7.50 (m, 2H), 7.38 (d, $^3J$ = 8.8 Hz, 2H) 7.38 (d, $^3J$ = 8.8 Hz, 2H), 7.24−7.28 (m, 2H), 2.01 (bs, 1H), 1.61 (s, 6H), 0.24 (s, 9H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 132.3, 131.7, 131.5 (2C), 128.2, 128.1, 125.7 (2C), 123.2, 122.7, 103.3, 98.7, 95.6, 92.9, 89.9, 81.8, 65.6, 31.4, 0.0 ppm. Anal. calcd for $C_{24}H_{24}OSi$: C, 80.85; H, 6.78. Found: C, 80.84; H, 6.88.

*Synthesis of Compound* ***6***. A solution of compound **16** (1.10 g, 3.09 mmol) in anhydrous PhMe (40 mL) was immersed in a preheated oil bath (130 °C). The reaction mixture was refluxed, and NaOH microgranules were added in one portion (135 mg, 3.39 mmol). The resultant mixture was stirred at 130 °C for 1 h. After completion (TLC), the reaction mixture was allowed to cool to room temperature. Then it was diluted with deionized water and extracted in PhMe (25 mL). The organic phase was washed with a saturated brine solution (75 mL) and dried over anhydrous $Na_2SO_4$. The solvent was removed in *vacuo* furnishing a brown oil that was purified by column chromatography on silica gel using *n*-hexane ($R_f$ = 0.15, $SiO_2$, *n*-hexane) yielding **6** as bright yellow solid (850 mg, 2.85 mmol, 92%). Mp: 55−56 °C. IR (KBr): $\nu$ 3291, 3056, 2958, 2152, 1913, 1797, 1597, 1499, 1404, 1318, 1244, 1092, 1033, 948, 846, 752, 660, 603, 503, 463 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.47−7.52 (m, 6H), 7.27−7.30 (m, 2H), 3.18 (s, 1H), 0.27 (s, 9H) ppm. $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 132.3, 132.0, 131.7, 131.5, 128.2, 128.1, 125.7 (2C), 123.8, 122.0, 103.3, 98.8, 92.8, 90.2, 83.3, 78.9, 0.0 ppm. Anal. calcd for $C_{21}H_{18}Si$: C, 84.51; H, 6.08. Found: C, 84.89; H, 6.08.

*Synthesis of Compound* ***17***. A solution of compounds **6** (369 mg, 1.24 mmol) and **7** (300 mg, 950 μmol) in anhydrous $Et_3N$ (60 mL) and THF (60 mL) was degassed using the freeze−pump−thaw procedure (3×). $Pd(PPh_3)_4$ (110 mg, 95.1 μmol) was added, and the reaction mixture was heated to 80 °C for 18 h (TLC). After evaporation of the solvents, deionized water (50 mL) was added and the residue was



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extracted in DCM (50 mL). The organic layer was dried over anhydrous $Na_2SO_4$ and evaporated. The yellow residue was purified by column chromatography on silica gel using gradient elution, 20% to 40% EtOAc in *n*-hexane ($R_f$ = 0.30, $SiO_2$, 60% EtOAc in DCM). Compound **17** was afforded as a pale yellow solid (370 mg, 280 $\mu$mol, 86%). Mp: 196−198 °C. IR (KBr): $\nu$ 3055, 2955, 2212, 2156, 1575, 1539, 1441, 1386, 1248, 1156, 1085, 1015, 842, 753, 697, 544, 536, 462 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 400 MHz): 9.33 (d, $^4J$ = 1.2 Hz, 1H), 8.93 (d, $^3J$ = 5.3 Hz, 1H), 8.87 (dd, $^4J$ = 2.2 Hz, $^5J$ = 0.8 Hz, 1H), 8.62 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.2 Hz, 1H), 8.60 (dd, $^3J$ = 8.0 Hz, $^4J$ = 1.2 Hz, 1H), 8.59 (dd, $^3J$ = 5.3 Hz, $^4J$ = 1.2 Hz, 1H), 8.57 (dd, $^3J$ = 8.1 Hz, $^5J$ = 1.2 Hz, 1H), 8.04 (t, $^3J$ = 8.0 Hz, $^3J$ = 8.0 Hz, 1H), 8.00 (dd, $^3J$ = 8.1 Hz, $^4J$ = 2.2 Hz, 1H), 7.58 (s, 4H), 7.51−7.54 (m, 2H), 7.31 (td, $^3J$ = 7.5 Hz, $^4J$ = 1.6 Hz, 1H), 7.29 (td, $^3J$ = 7.5 Hz, $^4J$ = 1.6 Hz, 1H), 0.27 (s, 9H) ppm. $^{13}C$ NMR ($CDCl_3$, 100 MHz): 162.7, 158.7, 157.9, 154.8, 154.1, 153.2, 151.4, 139.6, 138.3, 132.3, 131.7 (2C), 131.6, 128.3, 128.2, 125.7, 125.6, 123.9, 123.2, 122.3, 122.0, 120.6 (2C), 117.6, 103.3, 98.8, 93.7, 92.9, 90.5, 87.9, 0.0 ppm. ESI-MS: Calcd for $C_{35}H_{26}N_4Si$ $m/z$ (%) = 530.7. Found ($M{\cdot}H^+$): $m/z$ (%) = 531.8 (100).

*Synthesis of Compound* ***8***. Compound **17** (125 mg, 236 $\mu$mol) was dissolved in a solution of THF (60 mL) and MeOH (30 mL). Then aqueous KOH (40 mg, 0.70 mmol, in 5 mL deionized water) was added, and the reaction mixture was stirred at room temperature for 18 h (TLC). The solvent was removed, 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 ($R_f$ = 0.28, $SiO_2$, 60% EtOAc in DCM) to afford compound **8** as a yellow solid (90.0 mg, 200 $\mu$mol) in 85% yield. Mp: 202−204 °C. IR (KBr): $\nu$ 3259, 3039, 2995, 2212, 1905, 1575, 1441, 1389, 1250, 1081, 1017, 953, 824, 760, 632, 461, 535, 461 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 400 MHz): $\delta$ 9.29 (d, $^4J$ = 1.2 Hz, 1H), 8.89 (d, $^3J$ = 5.2 Hz, 1H), 8.86 (dd, $^4J$ = 2.1 Hz, $^5J$ = 0.8 Hz, 1H), 8.65 (dd, $^3J$ = 8.0, $^4J$ = 1.2 Hz, 1H), 8.60 (dd, $^3J$ = 8.0, $^4J$ = 1.2 Hz, 1H), 8.57 (dd, $^3J$ = 5.2, $^4J$ = 1.2 Hz, 1H), 8.55 (dd, $^3J$ = 8.2 Hz, $^5J$ = 1.2 Hz, 1H), 8.05 (t, $^3J$ = 8.0 Hz, $^3J$ = 8.0 Hz, 1H), 8.02 (dd, $^3J$ = 8.2 Hz, $^4J$ = 2.1 Hz, 1H), 7.60 (s, 4H), 7.55−7.59 (m, 2H), 7.39 (td, $^3J$ = 7.5 Hz, $^4J$ = 1.6 Hz, 1H), 7.34 (td, $^3J$ = 7.5 Hz, $^4J$ = 1.6 Hz, 1H), 3.47 (s, 1H) ppm. $^{13}C$ NMR ($CD_2Cl_2$, 100 MHz): $\delta$ 162.9, 159.1, 158.4, 155.5, 154.9, 153.6, 152.1, 139.7, 138.6, 133.0, 132.2, 132.1 (2C), 129.1, 128.7, 126.2, 125.0, 123.9, 123.3, 123.1, 122.1, 120.7 (2C), 117.7, 93.5, 93.2, 90.3, 88.6, 82.3, 81.6 ppm. Anal. calcd for $C_{32}H_{18}N_4{\cdot}1/7\ CH_2Cl_2$: C, 82.03; H, 3.92; N, 11.90. Found: C, 82.76; H, 3.92; N, 11.52. ESI-MS: Calcd for $C_{32}H_{18}N_4$ $m/z$ (%) = 458.5. Found ($M{\cdot}H^+$): $m/z$ (%) = 459.5 (100).

*Synthesis of Compound* ***19***. A mixture of compound **18** (5.00 g, 13.0 mmol), $PdCl_2(PPh_3)_2$ (450 mg, 625 $\mu$mol), and CuI (125 mg, 656 $\mu$mol) was placed in a tube. The tube was evacuated and filled with $N_2$ (3×) and predegassed anhydrous $Et_3N$ (70 mL). Trimethylsilylacetylene (2.80 mL, 19.4 mmol) was added, and the tube was sealed. The reaction mixture was vigorously stirred at room temperature for 3 h (TLC). The resulting mixture was filtered and washed with *n*-hexane (50 mL), and the solvent was evaporated in *vacuo*. The chromatographic purification on silica gel using *n*-hexane ($R_f$ = 0.59, $SiO_2$, 100% *n*-hexane) provided compound **19** as a white solid (1.10 g, 3.08 mmol, 23%). Mp: 91−92 °C. IR (KBr): $\nu$ 2953, 2400, 2141, 1536, 1450, 1413, 1373, 1289, 1247, 1208, 1077, 1009, 846, 757, 724, 702, 657, 501, 448 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 2.50 (s, 6H), 2.49 (s, 6H), 0.27 (s, 9H) ppm. $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 137.3, 136.4, 123.6, 112.4, 103.6, 102.8, 27.6, 20.2, 0.1 ppm. Calcd for $C_{15}H_{21}ISi$: C, 50.56; H, 5.94. Found: C, 50.55; H, 5.86.

*Synthesis of Compound* ***24***. Zinc(II)-5-(4′-ethynyl)phenyl-10,15,20-trimesitylporphyrin (**23**, 300 mg, 360 $\mu$mol) and compound **11** (710 mg, 1.10 mmol) were placed in an oven-dried 250 mL flask. Freshly distilled dry $Et_3N$ (40 mL) and dry DMF (40 mL) were added. After the mixture was sparged with nitrogen, $Pd(PPh_3)_4$ (42 mg, 0.036 mmol) was added, and the reaction mixture was heated to 80 °C for 36 h (TLC). The reaction mixture was cooled to rt, and solvents were removed under reduced pressure. The residue was dissolved in DCM (50 mL) and washed successively with deionized water (50 mL × 2) and brine (50 mL). The organic layer was dried over anhydrous $Na_2SO_4$. After removing the solvent under reduced pressure, the crude product was purified by column chromatography using 25% DCM in *n*-hexane on silica gel ($R_f$ = 0.25 $SiO_2$, 30% DCM in *n*-hexane). The obtained residue was further subjected to size exclusion chromatography on Biobeads-SX3 (Ø = 2 cm, $l$ = 55 cm) using toluene as an eluent. The pure fractions were combined and evaporated to afford compound **24** as a bright purple solid (495 mg, 350 $\mu$mol, 97%). Mp > 250 °C. IR (KBr): $\nu$ 3106, 2933, 2918, 2852, 2154, 1912, 1807, 1700, 1604, 1484, 1393, 1332, 1247, 1201, 1066, 999, 856, 806, 722, 650, 551, 411 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 400 MHz): $\delta$ 8.88 (d, $^3J$ = 4.6 Hz, 2H), 8.75 (d, $^3J$ = 4.6 Hz, 2H), 8.70 (s, 4H), 8.23 (d, $^3J$ = 8.3 Hz, 2H), 7.91 (d, $^3J$ = 8.3 Hz, 2H), 7.59 (d, $^3J$ = 8.6 Hz, 2H), 7.45 (d, $^3J$ = 8.6 Hz, 4H), 7.40 (d, $^3J$ = 8.6 Hz, 2H), 7.29 (s, 6H), 7.24 (d, $^3J$ = 8.6 Hz, 2H), 7.18 (d, $^3J$ = 8.6 Hz, 2H), 7.12 (d, $^3J$ = 8.6 Hz, 4H), 2.62 (s, 9H), 1.84 (s, 6H), 1.82 (s, 12H), 0.25 (s, 9H) ppm. $^{13}C$ NMR ($CD_2Cl_2$, 100 MHz): $\delta$ 150.3 (2C), 150.1, 150.0, 146.4, 146.2, 145.2, 143.6, 139.6, 139.5, 139.3 (2C), 137.9, 134.9, 133.0 (2C), 132.2, 131.8, 131.6, 131.5, 131.4 (2C), 131.3, 131.1, 131.0, 130.2, 128.0 (2C), 122.5, 121.9, 121.7, 120.9, 119.6, 119.3, 119.2, 104.8, 95.2, 90.3, 90.1, 64.7, 21.8, 21.7 (2C), 21.5, 0.0 ppm. Anal. calcd for $C_{85}H_{70}Br_2N_4SiZn{\cdot}PhMe$: C, 74.01; H, 5.27, N, 3.75. Found: C, 74.05; H, 5.46, N, 3.81.

*Synthesis of Compound* ***9***. A solution of compounds **24** (308 mg, 220 $\mu$mol) and **12** (50 mg, 110 $\mu$mol) in a mixture of freshly distilled anhydrous DMF (30 mL) and anhydrous $Et_3N$ (30 mL) was degassed using freeze−pump−thaw cycles (3×). After addition of $Pd(PPh_3)_4$ (13 mg, 11 $\mu$mol), the resulting mixture was heated to 80 °C for 36 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 washed sequentially 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 $Na_2SO_4$ and evaporated. The crude residue was purified by column chromatography with 15% EtOAc in *n*-hexane ($R_f$ = 0.35, $SiO_2$, 15% EtOAc in *n*-hexane) affording compound **9** as a bright purple solid in 76% yield (148 mg, 83.4 $\mu$mol). Mp > 250 °C. IR (KBr): $\nu$ 3032, 2955, 2915, 2854, 2374, 2155, 1609, 1584, 1491, 1438, 1376, 1335, 1248, 1203, 1061, 998, 864, 850, 825, 812, 799, 759, 722, 654, 548, 513 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 400 MHz): $\delta$ 8.91 (d, $^3J$ = 4.8 Hz, 2H), 8.76 (d, $^3J$ = 4.8 Hz, 2H), 8.71 (s, 4H), 8.34 (d, $^3J$ = 8.4 Hz, 1H), 8.33 (d, $^3J$ = 8.4 Hz, 1H), 8.23 (d, $^3J$ = 8.4 Hz, 2H), 7.92 (d, $^3J$ = 8.4 Hz, 2H), 7.90 (s, 2H), 7.62 (d, $^3J$ = 8.4 Hz, 2H), 7.57 (d, $^3J$ = 8.4 Hz, 1H), 7.56 ($^3J$ = 8.4 Hz, 2H), 7.57 (d, $^3J$ = 8.4 Hz, 1H), 7.48 (d, $^3J$ = 8.8 Hz, 2H), 7.43 (d, $^3J$ = 8.8 Hz, 2H), 7.28−7.32 (m, 10H), 7.25 (d, $^3J$ = 8.8 Hz, 2H), 7.19 (d, $^3J$ = 8.8 Hz, 2H), 6.97 (s, 2H), 2.62 (s, 9H), 2.54 (s, 6H), 2.34 (s, 3H), 2.05 (s, 6H), 1.95 (s, 6H), 1.85 (s, 6H), 1.83 (s, 12H), 0.26 (s, 9H) ppm. $^{13}C$ NMR ($CD_2Cl_2$, 100 MHz): $\delta$ 161.4, 160.5, 150.3 (2C), 150.1, 150.0, 146.7 (2C), 146.6, 146.5, 145.9, 145.4, 143.6, 142.0, 139.6, 139.5, 139.3 (2C), 138.5, 137.9, 137.8, 136.6, 136.5, 136.4, 136.1, 134.9 (2C), 133.1, 132.2 (2C), 131.7, 131.6, 131.5 (2C), 131.4 (2C), 131.3 (2C), 131.2 (2C), 131.0, 130.1, 128.6, 128.0, 127.6 (2C), 126.7, 126.5, 124.9, 124.8, 123.1, 122.6 (2C), 121.8, 121.6, 120.8, 119.6, 119.3, 119.2, 104.9, 96.8, 95.1, 90.2, 90.1, 89.7, 65.0, 21.8, 21.7 (2C), 21.5, 21.2, 20.4, 18.6, 17.7, 0.0 ppm. Anal. calcd for $C_{118}H_{99}BrN_6SiZn{\cdot}EtOAc$: C, 78.67; H, 5.79; N, 4.51. Found: 78.61; H, 5.52; N, 4.62. ESI-MS: Calcd for $C_{118}H_{99}BrN_6SiZn$ $m/z$ (%) = 1774.5. Found: $[M{\cdot}H]^+$ $m/z$ (%) = 1775.1 (100); $[M{\cdot}2H]^{2+}$ $m/z$ = 888.2 (26).

*Synthesis of Compound* ***25***. To a solution of compounds **9** (193 mg, 109 $\mu$mol) and **8** (50.0 mg, 109 $\mu$mol) were added freshly distilled anhydrous DMF (30 mL) and anhydrous $Et_3N$ (30 mL). The reaction mixture was degassed using freeze−pump−thaw cycles (3×). $Pd(PPh_3)_4$ (13 mg, 11 $\mu$mol) was added, and reaction mixture was further subjected to freeze−pump−thaw cycles (3×). $^tBu_3PHBF_4$ (3.0 mg, 10.0 $\mu$mol) was added under nitrogen, and the resulting mixture was heated to 80 °C for 24 h under an inert atmosphere. The reaction mixture was allowed to cool to room temperature. The reaction was further subjected to freeze−pump−thaw cycles (2×). $Pd(PPh_3)_4$ (6.5 mg, 5.5 $\mu$mol) and $^tBu_3PHBF_4$ (1.5 mg, 5.0 $\mu$mol) were added, and the reaction was further heated at 80 °C for 26 h (TLC control). The solvent was evaporated in *vacuo*. The residue was dissolved in DCM (25 mL) and washed sequentially with deionized water (25 mL × 2) and a saturated brine solution


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(25 mL × 3). The organic layer was removed, and the aqueous layer was re-extracted with DCM (25 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, and the solvent was removed. The crude residue was purified by column chromatography (Ø = 2 cm, $l$ = 10 cm) using 15% EtOAc in DCM ($R_f$ = 0.30, $SiO_2$, 30% EtOAc in DCM) to afford a purple solid. The crude product was further purified by size-exclusion chromatography on Biobeads-SX3 (Ø = 2 cm, $l$ = 55 cm) using toluene as an eluent. All fractions were analyzed by $^1$H NMR, and fractions with pure compound were combined. After evaporation of the solvent, the title compound **25**[27] was obtained as a purple solid (105 mg, 36.7 μmol, 45%). Mp > 300 °C. IR (KBr): $\nu$ 3032, 2915, 2728, 2207, 2153, 1915, 1805, 1716, 1580, 1501, 1442, 1379, 1331, 1248, 1201, 1062, 997, 823, 755, 653, 544 cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$, 600 MHz): $\delta$ 8.85 (d, $^3J$ = 4.6 Hz, 2H), 8.71 (d, $^3J$ = 4.6 Hz, 2H), 8.68 (d, $^4J$ = 2.1 Hz, 1H), 8.66 (d, $^3J$ = 4.6 Hz, 2H), 8.64 (d, $^3J$ = 4.6 Hz, 2H), 8.35 (d, $^3J$ = 8.2 Hz, 1H), 8.34 (d, $^3J$ = 8.2 Hz, 1H), 8.26 (d, $^3J$ = 8.1 Hz, 2H), 8.20 (dd, $^3J$ = 7.8 Hz, $^3J$ = 7.8 Hz, 1H), 8.15 (d, $^3J$ = 8.0 Hz, 1H), 7.95 (d, $^3J$ = 8.1 Hz, 2H), 7.91 (s, 2H), 7.87 (dd, $^3J$ = 8.0 Hz, $^4J$ = 2.1 Hz, 1H), 7.66 (d, $^3J$ = 8.4 Hz, 2H), 7.54−7.63 (m, 14H), 7.44 (d, $^3J$ = 8.4 Hz, 2H), 7.36−7.38 (m, 4H), 7.35 (d, $^3J$ = 8.6 Hz, 2H), 7.33 (s, 2H), 7.29 (d, $^3J$ = 8.6 Hz, 2H), 7.27 (d, $^3J$ = 8.6 Hz, 2H), 7.24 (s, 4H), 6.96 (s, 2H), 6.85 (dd, $^3J$ = 5.8 Hz, $^5J$ = 1.0 Hz, 1H), 3.76 (s, 1H), 2.73 (d, $^3J$ = 5.8 Hz, 1H), 2.64 (s, 3H), 2.58 (s, 6H), 2.54 (s, 6H), 2.33 (s, 3H), 2.04 (s, 6H), 1.92 (s, 12H), 1.74 (s, 12H), 0.26 (s, 9H) ppm. $^{13}$C NMR ($CD_2Cl_2$, 100 MHz): $\delta$ 162.5, 161.4, 160.5, 155.0, 154.3, 153.0, 151.5, 151.3 (2C), 150.2, 150.1, 149.9, 149.8, 146.8, 146.7 (2C), 146.5, 146.0, 144.1, 142.0, 140.1, 139.8 (2C), 139.6, 139.5, 138.5, 138.1, 137.8, 137.7, 137.6, 136.6, 136.4, 136.3, 136.1, 135.1, 132.6, 132.3, 132.2 (2C), 132.1, 132.0 (2C), 131.8, 131.6, 131.5 (3C), 131.3 (2C), 131.2 (2C), 130.9, 130.1, 128.8, 128.6 (2C), 127.9, 127.8, 127.6 (2C), 126.5, 126.1, 125.5, 124.9, 124.8, 124.0, 123.1, 123.0, 122.9, 122.6 (2C), 122.3, 121.8, 121.6 (2C), 121.4, 120.7, 120.6, 119.0, 118.9 (2C), 118.8, 115.9, 104.9, 96.8, 95.1, 93.8, 93.6, 93.3, 90.8, 90.3, 90.1, 89.7, 88.7, 88.6, 65.4, 22.0, 21.8, 21.6, 21.5, 21.2, 20.4, 18.6, 17.7, 0.0 ppm. Anal. calcd for $C_{150}H_{116}N_{10}SiZn{\cdot}MeCO_2Et$: C, 82.57; H, 5.58; N, 6.25. Found: C, 82.34; H, 5.29; N, 6.13. UV−vis: $\lambda_{max}$ = 429 nm. ESI-MS: Calcd for $C_{150}H_{116}N_{10}SiZn$ $m/z$ (%) = 2152.1. Found (M·2H$^+$/2): $m/z$ (%) = 1076.9 (100).

*Synthesis of Compound* ***4***. To a solution of compound **25** (130 mg, 60.4 μmol) in THF−MeOH (v/v, 3:1, 40 mL) was added a solution of KOH (51 mg, 0.91 mmol in 10 mL of $H_2O$). The reaction mixture was allowed to stir at room temperature overnight. The solvent was evaporated under reduced pressure. The residue was extracted in DCM (20 mL) and washed with $H_2O$ (20 mL × 2). The organic layer was dried over anhydrous $Na_2SO_4$. The evaporation of solvent afforded compound **4** as a purple solid (120 mg, 57.7 μmol, 96% yield). Mp > 250 °C. IR: $\nu$ 2955, 2917, 2854, 2211, 2154, 2103, 1901, 1583, 1479, 1446, 1389, 1247, 1203, 1097, 1064, 1002, 882, 760, 628, 518 cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$, 400 MHz): $\delta$ 8.85 (d, $^3J$ = 4.6 Hz, 2H), 8.71 (d, $^3J$ = 4.6 Hz, 2H), 8.68 (d, $^4J$ = 2.1 Hz, 1H), 8.66 (d, $^3J$ = 4.6 Hz, 2H), 8.64 (d, $^3J$ = 4.6 Hz, 2H), 8.35 (d, $^3J$ = 8.0 Hz, 1H), 8.34 (d, $^3J$ = 8.0 Hz, 1H), 8.26 (d, $^3J$ = 8.3 Hz, 2H), 8.26 (dd, $^3J$ = 7.8 Hz, 1H), 8.16 (d, $^3J$ = 8.0 Hz, 1H), 7.95 (d, $^3J$ = 8.3 Hz, 2H), 7.91 (dd, $^3J$ = 8.0 Hz, $^4J$ = 2.1 Hz, 1H), 7.90 (s, 2H), 7.67 (d, $^3J$ = 8.6 Hz, 2H), 7.53−7.64 (m, 14H), 7.48 (d, $^3J$ = 8.6 Hz, 2H), 7.34−7.39 (m, 6H), 7.32 (s, 2H), 7.30 (d, $^3J$ = 8.4 Hz, 2H), 7.29 (d, $^3J$ = 8.4 Hz, 2H), 7.24 (s, 4H), 6.96 (s, 2H), 6.87 (dd, $^3J$ = 5.8 Hz, $^5J$ = 1.0 Hz, 1H), 3.87 (s, 1H), 3.16 (s, 1H), 2.86 (d, $^3J$ = 5.8 Hz, 1H), 2.64 (s, 3H), 2.58 (s, 6H), 2.54 (s, 6H), 2.34 (s, 3H), 2.04 (s, 6H), 1.94 (s, 12H), 1.74 (s, 12H) ppm. $^{13}$CNMR ($CD_2Cl_2$, 100 MHz): $\delta$ 162.6, 161.4, 160.5, 155.1, 154.4, 153.1, 151.6, 151.5, 151.2, 150.2 (2C), 149.9, 149.7, 147.1, 146.7 (2C), 146.4, 146.0, 144.1, 142.0, 140.3, 139.8 (2C), 139.6, 139.5, 138.5, 138.3, 137.8, 137.7, 137.6, 136.6, 136.4, 136.3, 136.1, 135.1, 132.7, 132.3, 132.2, 132.1, 132.0 (3C), 131.6, 131.5 (2C), 131.3 (2C), 131.2 (2C), 130.9, 130.1, 128.9, 128.8, 128.6 (2C), 127.9, 127.8, 127.6 (2C), 126.6, 126.5, 126.1, 125.4, 124.9, 124.8, 124.1, 123.1, 123.0, 122.9, 122.6, 122.3, 121.8, 121.6 (2C), 121.4, 120.7 (2C), 120.5, 118.9 (3C), 118.8, 116.0, 96.8, 93.8, 93.5, 93.2, 90.7, 90.3, 90.1, 89.7, 88.7, 88.6, 83.5, 77.8, 65.4, 22.0, 21.7, 21.5 (2C), 21.2, 20.4, 18.6, 17.7 ppm. Anal. calcd for $C_{147}H_{108}N_{10}Zn{\cdot}1/2\ CH_2Cl_2$: C, 83.47; H, 5.18; N, 6.60. Found: C, 83.87; H, 5.06; N, 6.47. ESI-MS: Calcd for $C_{147}H_{108}N_{10}Zn$ $m/z$ (%) = 2079.9. Found [M·2H]$^{2+}$: $m/z$ (%) = 1041.2 (100).

*Synthesis of Compound* ***1*** *= State I*. A solution of compounds **4** (40.0 mg, 19.2 μmol) and **5** (32.0 mg, 58.0 μmol) in a mixture of freshly distilled anhydrous $Et_3N$ (20 mL) and anhydrous DMF (20 mL) was degassed using freeze−pump−thaw cycles (3×). After addition of $Pd(PPh_3)_4$ (4.50 mg, 3.90 μmol), the reaction mixture was further subjected to freeze−pump−thaw cycles (2×). The resulting mixture was stirred at 60 °C for 24 h. The solvent was evaporated in *vacuo*. The residue was dissolved in DCM (20 mL) and washed with deionized water (10 mL × 2) and a saturated brine solution (10 mL × 2). The organic layer was removed, and the aqueous layer was re-extracted in DCM (10 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$, and the solvent was removed. The purple residue was subjected to column chromatography (Ø = 3 cm, $l$ = 15 cm) using 25% EtOAc in DCM ($R_f$ = 0.20, $SiO_2$, 30% EtOAc in DCM) to furnish a purple solid. The crude product was further subjected to size-exclusion chromatography on Biobeads-SX3 (Ø = 2 cm, $l$ = 55 cm) using toluene as an eluent. All fractions were analyzed by $^1$H NMR. Fractions with pure compound were combined, and the residue was triturated in *n*-pentane. The solvent was removed in *vacuo* to afford compound **1** as a purple solid (25.0 mg, 9.97 μmol, 52%). Mp > 300 °C. IR (KBr): $\nu$ 3027, 2907, 2712, 2201, 1917, 1723, 1577, 1503, 1442, 1386, 1334, 1249, 1207, 1069, 999, 820, 758, 646, 607, 537 cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$, 600 MHz): $\delta$ 8.86 (d, $^3J$ = 4.5 Hz, 2H), 8.71 (d, $^3J$ = 4.5 Hz, 2H), 8.68 (dd, $^4J$ = 2.2 Hz, 1H), 8.66 (d, $^3J$ = 4.5 Hz, 2H), 8.64 (d, $^3J$ = 4.5 Hz, 2H), 8.36 (d, $^3J$ = 7.8 Hz, 2H), 8.34 (d, $^3J$ = 7.8 Hz, 2H), 8.26 (d, $^3J$ = 8.4 Hz, 2H), 8.20 (dd, $^3J$ = 7.7 Hz, $^3J$ = 7.7 Hz, 1H), 8.16 (d, $^3J$ = 8.0 Hz, 1H), 7.96 (d, $^3J$ = 8.4 Hz, 2H), 7.92 (dd, $^3J$ = 8.0 Hz, $^4J$ = 2.2 Hz, 1H), 7.91 (s, 4H), 7.69 (d, $^3J$ = 8.3 Hz, 2H), 7.54−7.65 (m, 16H), 7.44 (m, 1H), 7.43 (d, $^3J$ = 8.3 Hz, 2H), 7.40 (d, $^3J$ = 8.3 Hz, 2H), 7.34−7.38 (m, 3H), 7.35 ($^3J$ = 8.4 Hz, 4H), 7.33 (s, 2H), 7.24 (s, 4H), 6.96 (s, 4H), 6.84 (dd, $^3J$ = 5.8 Hz, $^5J$ = 1.0 Hz, 1H), 3.74 (s, 1H), 2.70 (d, $^3J$ = 5.8 Hz, 1H), 2.64 (s, 3H), 2.58 (s, 6H), 2.54 (s, 12H), 2.34 (s, 6H), 2.05 (s, 12H), 1.95 (s, 18H), 1.74 (s, 12H) ppm. $^{13}$C NMR ($CD_2Cl_2$, 100 MHz): $\delta$ 162.6, 161.5, 160.5, 155.0, 154.4, 152.9, 151.4 (2C), 151.2, 150.2 (2C), 149.9, 149.7, 146.9, 146.7 (2C), 146.6, 146.2 (2C), 144.1, 142.0, 140.3, 139.8 (2C), 139.6, 139.5, 138.5, 138.2 (2C), 137.8, 137.7, 137.6, 136.6, 136.4, 136.3, 136.1, 135.1, 132.7, 132.3, 132.2 (2C), 132.0 (2C), 131.6, 131.5 (2C), 131.4, 131.3, 131.2 (2C), 130.9, 130.1, 128.9, 128.6 (2C), 127.9, 127.8, 127.6 (2C), 126.6, 126.5, 126.1, 125.4, 124.9, 124.8, 124.1, 123.1, 122.9 (2C), 122.5, 122.3, 121.7, 121.6, 121.3, 120.7, 118.9 (2C), 118.8, 116.0, 96.9, 93.9, 93.6, 93.2, 90.7, 90.2, 90.1, 89.7, 88.7, 88.6, 65.4, 22.0, 21.7, 21.6, 21.5, 21.2, 20.4, 18.6, 17.7 ppm. Anal. calcd for $C_{178}H_{136}N_{12}Zn{\cdot}CH_2Cl_2$: C, 82.90; H, 5.36; N, 6.48. Found: C, 82.53; H, 5.56; N, 6.22. ESI-MS: Calcd for $C_{178}H_{136}N_{12}Zn$ $m/z$ (%) = 2508.2. Found [M·2H]$^{2+}$: $m/z$ (%) = 1255.4 (100).

*Synthesis of Complex [Cu(***1***)]$^+$ = State II*. Nanoswitch **1** (508 μg, 203 μmol) and $[Cu(CH_3CN)_4B(C_6F_5)_4]$ (0.184 μg, 203 μmol) were combined in an NMR tube. $CD_2Cl_2$ was added to this mixture, and the $^1$H NMR was recorded. Yield: Quantitative (two diastereomers 55:45).

Mp > 250 °C. IR (KBr): $\nu$ 3030, 2917, 2865, 2323, 2221, 1700, 1642, 1582, 1510, 1461, 1379, 1334, 1274, 1203, 1086, 996, 978, 889, 821, 801, 771, 754, 723, 684, 661, 640, 606 cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$, 600 MHz): $\delta$ 8.90 (d, $^3J$ = 4.6 Hz, 0.9H), 8.88 (d, $^3J$ = 4.6 Hz, 1.1H), 8.77 (d, $^3J$ = 4.6 Hz, 1.1H), 8.75 (d, $^3J$ = 4.6 Hz, 0.9H), 8.74 (d, $^3J$ = 8.2 Hz, 1H), 8.69−8.72 (m, 4H), 8.47 (d, $^3J$ = 8.2 Hz, 1H), 8.33−8.38 (m, 2H), 8.26 (d, $^3J$ = 8.2 Hz, 1H), 8.24 (d, $^3J$ = 8.2 Hz, 1H), 8.22 (d, $^3J$ = 8.2 Hz, 1H), 8.12 (d, $^3J$ = 8.2 Hz, 1H), 8.09−8.12 (m, 2H), 7.99 (d, $^3J$ = 8.2 Hz, 1H), 7.91−7.96 (m, 8H), 7.83−7.84 (m, 1H), 7.71 (2 d, $^3J$ = 8.2 Hz, 1H), 7.67 (d, $^3J$ = 8.4 Hz, 1H), 7.65 (d, $^3J$ = 8.4 Hz, 1H), 7.53−7.62 (m, 11H), 7.49 (d, $^3J$ = 8.4 Hz, 1H), 7.33−7.45 (m, 13H), 7.30 (s, 2H), 7.29 (s, 4H), 7.26 (d, $^3J$ = 4.8 Hz, 1H), 6.97 (s, 0.9H), 6.95 (s, 1.1H), 6.30 (s, 2H), 2.62 (2 s, 9H), 2.57 (s, 3.3H), 2.54 (s, 2.7H), 2.50 (s, 3.3H), 2.33 (2 s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3.3H), 1.95 (s, 2.7H), 1.93 (s, 2.7H), 1.92 (s, 3H), 1.84 (s, 12H), 1.83 (s, 6H), 1.80 (s, 2.7H), 1.69 (s, 3.3H), 1.52 (s, 3H) ppm. Anal. calcd for $C_{202}H_{136}BCuF_{20}N_{12}Zn{\cdot}2CH_2Cl_2{\cdot}H_2O$: C, 71.25; H, 4.16; N, 4.89. Found: C, 71.02; H, 3.95; N, 4.56. ESI-MS: Calcd For $[C_{178}H_{136}CuN_{12}Zn{\cdot}MeOH{\cdot}H_2O]^+$: $m/z$ (%) = 2622.0. Found: [Cu(**1**)·MeOH·H$_2$O]$^+$ $m/z$ (%) = 2623.4 (100); [Cu(**1**)·MeOH·(H$_2$O)$_2$]$^{2+}$ $m/z$ (%) = 1319.9 (16).



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*Synthesis of Complex $[Cu_2(1)(2)]^{2+}$ = State IV.* To a solution of State II (518 μg, 206 μmol) in $CD_2Cl_2$ was added [1,10]-phenanthroline (37 μg, 206 μmol). The formation of State III was confirmed by $^1H$ NMR. Then, $[Cu(CH_3CN)_4B(C_6F_5)_4]$ (0.187 μg, 206 μmol) was added, and the mixture was sonicated at 40 °C for 10 min. Thereafter, $^1H$ NMR was measured without further purification. Yield: Quantitative.

Mp > 300 °C. IR (KBr): ν 2918, 2317, 2215, 2114, 1734, 1696, 1642, 1576, 1559, 1510, 1460, 1424, 1374, 1336, 1274, 1204, 1142, 1084, 1017, 996, 866, 838, 824, 774, 755, 682, 660, 639, 603 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 400 MHz): δ 8.90 (d, $^3J$ = 4.8 Hz, 1H), 8.89 (d, $^3J$ = 4.8 Hz, 1H), 8.77 (d, $^3J$ = 4.8 Hz, 1H), 8.75 (d, $^3J$ = 4.8 Hz, 1H), 8.62−8.73 (m, 7H), 8.46−8.49 (m, 3H), 8.40 (dd, $^3J$ = 8.1 Hz, $^4J$ = 1.5 Hz, 2H), 8.26 (2 d, $^3J$ = 8.0 Hz, 2H), 8.17−8.22 (m, 3H), 8.02−8.12 (m, 3H), 7.91−7.98 (m, 3H), 7.85−7.90 (m, 6H), 7.77−7.82 (m, 3H), 7.68−7.74 (m, 5H), 7.63 (d, $^3J$ = 8.4 Hz, 2H), 7.56−7.62 (m, 6H), 7.33−7.51 (m, 15H), 7.30 (s, 2H), 7.28 (s, 4H), 7.24 (d, $^3J$ = 4.8 Hz, 1H), 6.29 (2 s, 2H), 6.02 (s, 0.7H), 6.02 (s, 1.3H), 2.62 (s, 3H), 2.61 (s, 6H), 2.49 (s, 3H), 1.92 (s, 3H), 1.83 (s, 12H), 1.82 (s, 6H), 1.79 (s, 3H), 1.79 (2 s, 6H), 1.77 (s, 3H), 1.70 (s, 3H), 1.69 (s, 3H), 1.60 (2 s, 6H), 1.53−1.57 (m, 12H) ppm. Anal. calcd for $C_{238}H_{144}B_2Cu_2F_{40}N_{14}Zn{\cdot}2CH_2Cl_2$: C, 66.36; H, 3.43; N, 4.51. Found: C, 66.29; H, 3.35; N, 4.26. ESI-MS: Calcd for $[C_{190}H_{144}Cu_2N_{14}Zn]^{2+} = [Cu_2(\mathbf{1})(\mathbf{2})]^{2+}$: $m/z$ (%) = 1407.8. Found $m/z$ (%) = 1407.9 (100).

*Synthesis of Complex $[Cu_2(1)(2)_2]^{2+}$ = State V.* To a solution of preprepared State IV (913 μg, 203 μmol) in $CD_2Cl_2$ was added [1,10]-phenanthroline (36.5 μg, 203 μmol). Subsequently, $^1H$ NMR was measured without further purification. Yield: Quantitative.

Mp > 300 °C. IR (KBr): ν 2917, 2857, 2362, 2323, 2214, 2097, 1922, 1696, 1642, 1585, 1558, 1510, 1461, 1424, 1374, 1335, 1273, 1222, 1142, 1084, 995, 977, 866, 838, 822, 799, 774, 768, 755, 725, 682, 660, 639, 605 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 400 MHz): δ 8.85 (d, $^3J$ = 4.6 Hz, 2H), 8.72 (d, $^3J$ = 4.6 Hz, 2H), 8.72 (d, $^3J$ = 8.0 Hz, 2H), 8.69 (dd, $^4J$ = 2.1 Hz, 1H), 8.72 (d, $^3J$ = 8.0 Hz, 2H), 8.66 (d, $^3J$ = 4.6 Hz, 2H), 8.65 (d, $^3J$ = 4.6 Hz, 2H), 8.48 (dd, $^3J$ = 4.7 Hz, $^4J$ = 1.6 Hz, 4H), 8.40 (dd, $^3J$ = 8.1 Hz, $^4J$ = 1.6 Hz, 4H), 8.29 (d, $^3J$ = 8.1 Hz, 2H), 8.21 (dd, $^3J$ = 7.8 Hz, $^3J$ = 7.8 Hz, 1H), 8.20 (s, 4H), 8.18 (d, $^3J$ = 8.0 Hz, 1H), 7.97 (d, $^3J$ = 8.1 Hz, 2H), 7.93 (dd, $^3J$ = 8.0 Hz, $^4J$ = 2.1 Hz, 1H), 7.88 (d, $^3J$ = 8.0 Hz, 2H), 7.86 (s, 4H), 7.84 (d, $^3J$ = 8.0 Hz, 2H), 7.72 (d, $^3J$ = 8.8 Hz, 2H), 7.70s (dd, $^3J$ = 8.1, $^3J$ = 4.7 Hz, 4H), 7.59−7.67 (m, 8H), 7.37−7.48 (m, 16H), 7.33 (s, 2H), 7.24 (s, 4H), 6.85 (dd, $^3J$ = 5.8 Hz, $^4J$ = 1.0 Hz, 1H), 6.02 (s, 4H), 3.74 (s, 1H), 2.68 (d, $^3J$ = 5.8 Hz, 1H), 2.64 (s, 3H), 2.58 (s, 6H), 1.95 (s, 6H), 1.78 (s, 12H), 1.74 (s, 12H), 1.69 (s, 12H), 1.59 (s, 12H), 1.56 (s, 6H) ppm. Anal. calcd for $C_{250}H_{152}B_2Cu_2F_{40}N_{16}Zn{\cdot}2CH_2Cl_2$: C, 66.90; H, 3.48; N, 4.95. Found: C, 66.55; H, 3.38; N, 4.67. ESI-MS: Calcd for $[C_{202}H_{152}Cu_2N_{16}Zn]^{2+} = [Cu_2(\mathbf{1})(\mathbf{2})_2]^{2+}$: $m/z$ (%) = 1498.0. Found: $m/z$ (%) = 1498.9 (100).

*Synthesis of Complex $[Cu_2(1)]^{2+}$.* Nanoswitch **1** (1.04 mg, 414 μmol) and $[Cu(CH_3CN)_4B(C_6F_5)_4]$ (0.751 μg, 828 μmol) were placed in an NMR tube. To this mixture $CD_2Cl_2$ was added, and the $^1H$ NMR was recorded. Yield: Quantitative.

Mp > 300 °C. IR (KBr): ν 2916, 2855, 2321, 2214, 2217, 2082, 1641, 1582, 1509, 1459, 1377, 1332, 1273, 1248, 1202, 1084, 1017, 996, 976, 817, 800, 770, 753, 722, 682, 658, 607, 542 $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 400 MHz): δ 8.87−8.92 (m, 2H), 8.74−8.78 (m, 2H), 8.66−8.72 (m, 5H), 8.43 (d, $^3J$ = 8.8 Hz, 1H), 8.31−8.36 (m, 2H), 8.23−8.27 (m, 2H), 8.09−8.16 (m, 2H), 7.98−8.15 (m, 2H), 7.84−7.98 (m, 9H), 7.67−7.73 (m, 2H), 7.51−7.67 (m, 15H), 7.26−7.48 (m, 19H), 7.23 (s, 1H), 7.00 (s, 2H), 6.28 (s, 2H), 2.62 (s, 9H), 2.55 (s, 3H), 2.53 (s, 3H), 2.49 (s, 3H), 2.33 (s, 3H), 2.02 (s, 12H), 1.99 (s, 3H), 1.95 (s, 3H), 1.93 (s, 3H), 1.90 (s, 3H), 1.83 (2 s, 18H), 1.75 (s, 3H), 1.70 (s, 3H) ppm. Anal. calcd for $C_{226}H_{136}B_2Cu_2F_{40}N_{12}Zn{\cdot}CH_3CN{\cdot}CH_2Cl_2$: C, 66.76; H, 3.45; N, 4.42. Found: C, 66.64; H, 3.36; N, 4.68. ESI-MS: Calcd for $[C_{178}H_{136}Cu_2N_{12}Zn]^{2+} = [Cu_2(\mathbf{1})]^{2+}$: $m/z$ (%) = 1317.7. Found: $m/z$ (%) = 1317.9 (100).

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02436.

Experimental procedures, NMR and ESI−MS spectra, UV−vis titrations (PDF)

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### Notes

The authors declare no competing financial interest.

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