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Synthesis of [3]Rotaxanes by the Combination of Copper-Mediated Coupling Reaction and Metal-Template Approach

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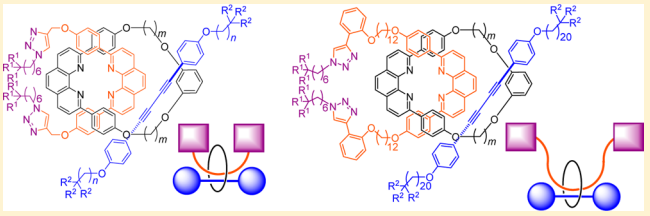
Supporting Information

ABSTRACT: [3]Rotaxanes with two axle components and one ring component were synthesized by the combination of a coupling reaction using a transition-metal catalyst and a metal-template approach. Thus, [2]rotaxanes were prepared by the oxidative dimerization of alkyne promoted by macrocyclic phenanthroline−CuI complexes. The [2]rotaxane was reacted with a Cu^{I} salt and an acyclic ligand to generate a tetrahedral Cu^{I} complex. Metal-free [3]rotaxane was isolated by the end-capping reaction of the acyclic ligand, followed by the removal of Cu^{I} ion. The stability of the tetrahedral Cu^{I} complexes depended on the size of both the ring component and the acyclic ligand, which was correlated with the yield of the corresponding [3]rotaxane.



INTRODUCTION

The chemistry of interlocked compounds such as [2]rotaxanes have attracted great interest for decades, and many synthetic methods such as template synthesis, self-assembly, or metal-catalyzed coupling reaction have been developed.[1] Since interlocked compounds are the promising candidates for the components of molecular machines, the understanding of the synthesis as well as the structure of these compounds is a very important issue. Along with the remarkable progress of the chemistry of [2]rotaxanes, the studies related to the chemistry of complex interlocked compounds such as [3]rotaxane were intensively carried out (Figure 1).[2−5] There are many synthetic

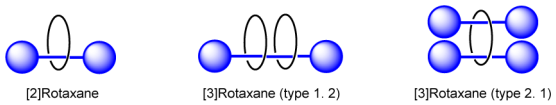


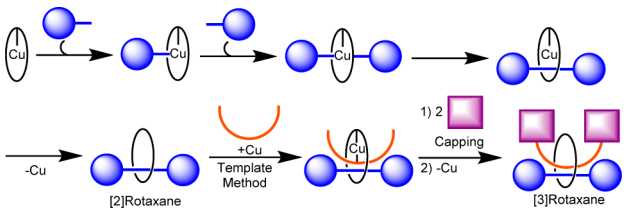
Figure 1. Structure of [2] and [3]rotaxanes.

methods of [3]rotaxane with one axle component and two ring components (Type 1.2),[2] while [3]rotaxane (Type 2.1)[3] with two axle components passing through one ring component remain very rare: further studies are required to understand the chemistry of these complex interlocked compounds.[4]

Recently, we reported the synthesis of rotacatenanes, which were composed of a [2]rotaxane component and a ring component.[6] In our synthesis, the coordination ability of a macrocyclic phenanthroline was utilized for both the synthesis of a [2]rotaxane[7−9] and the installation of another ring component.[10,11] For the synthesis of a [2]rotaxane, the catalytic activity of the macrocyclic phenanthroline−Cu complex was utilized. This synthetic approach was initially reported by Leigh's group using a macrocyclic pyridine−Cu complex.[8] We have been independently studying a similar synthetic approach and reported the synthesis of [2]rotaxanes using the macrocyclic phenanthroline−Cu complex.[9] As for the installation of another ring component, the metal-template method, which was originally developed by Sauvage, Dietrich-Buchecker, and co-workers[11] and applied to the synthesis of a [2]rotaxane by Gibson and co-workers,[12a] was employed. The combination of a copper-mediated catalytic threading approach (also known as active-metal template approach)[13] and a metal-template method turned out to be an efficient method for the synthesis of rotacatenane.

The successful synthesis of rotacatenanes prompted us to synthesize a [3]rotaxane (Type 2.1). Our synthetic strategy of [3]rotaxane is summarized in Scheme 1. A [2]rotaxane is prepared by the oxidative coupling of alkyne using a macrocyclic phenanthroline−CuI complex.[4e,6,7m,9] The installation of the second axle is achieved by the metal-template approach,[12] and metal-free [3]rotaxanes would be isolated after

Scheme 1. A Strategy for the Synthesis of [3]Rotaxanes



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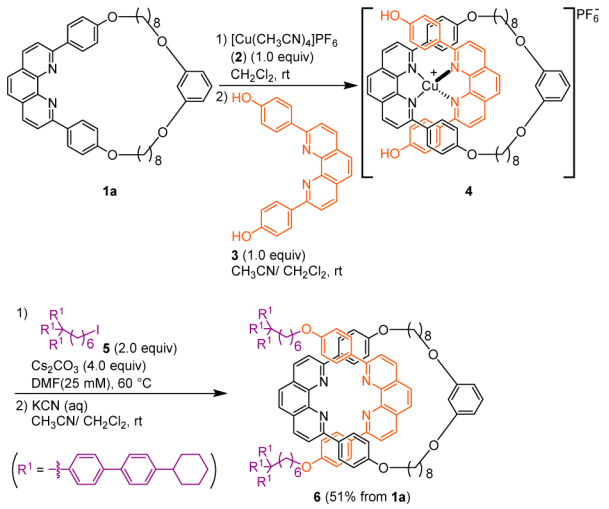
the removal of the metal. In this paper, we report the synthesis of [3]rotaxanes by the above-mentioned strategy.

RESULTS AND DISCUSSION

Synthesis of [2] and [3]Rotaxanes Using Williamson Ether Synthesis. We started our study by synthesizing [2]rotaxanes from a 37-membered macrocyclic phenanthroline (**1a**),[6,7m,12f] which we consider as the model system for the synthesis of [3]rotaxane. In order to introduce a bulky substituent at final stage of the synthesis of rotaxane, we employed Williamson ether synthesis as the end-capping reaction.[7m,12a,b,f] The result of the synthesis of [2]rotaxane is summarized in Scheme 2. A tetrahedral Cu^{I} complex (**4**) was

Scheme 2. Synthesis of a [2]Rotaxane by Williamson Ether Synthesis

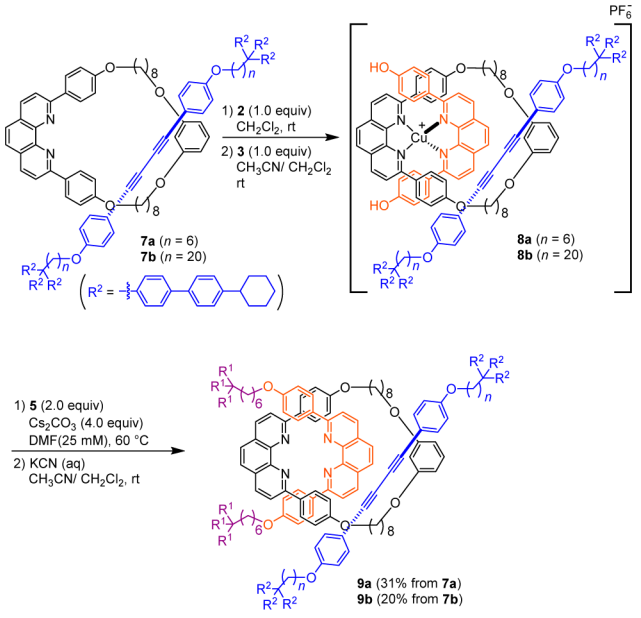


prepared *in situ* from **1a**, $[Cu(CH_3CN)_4]PF_6$ (**2**), and a phenanthroline derivative (**3**),[11] and the reaction of **4** with an iodoalkane with a bulky blocking group (**5**)[7m] proceeded in the presence of Cs_2CO_3. The crude product was treated with an excess amount of KCN to remove Cu^{I} ion from the phenanthroline ligand, and the corresponding [2]rotaxane **6** was isolated in 51% yield.[14]

With this successful result in hand, we synthesized [3]rotaxanes from [2]rotaxane **7a** (n = 6) or **7b** (n = 20) with 37-membered macrocyclic phenanthroline.[4e,6,7m] The results are summarized in Scheme 3. When [2]rotaxane **7a** was used as a substrate, [3]rotaxane **9a** was obtained in 31% yield. [2]Rotaxane **7b** with a longer methylene tether also reacted under similar conditions, and the corresponding [3]rotaxane **9b** was isolated in 20% yield. The yields of the [3]rotaxanes (**9a,b**) were lower compared to the yield of the corresponding [2]rotaxane (**6**, 51% yield). The low yields of [3]rotaxane **9** might be due to the dissociation of **3** from tetrahedral Cu^{I} complexes **8a,b**, which proceeded at the high temperature required for Williamson ether synthesis: the presence of an axle moiety in the macrocyclic phenanthroline ring would reduce the stability of the tetrahedral complex by the steric hindrance.[15]

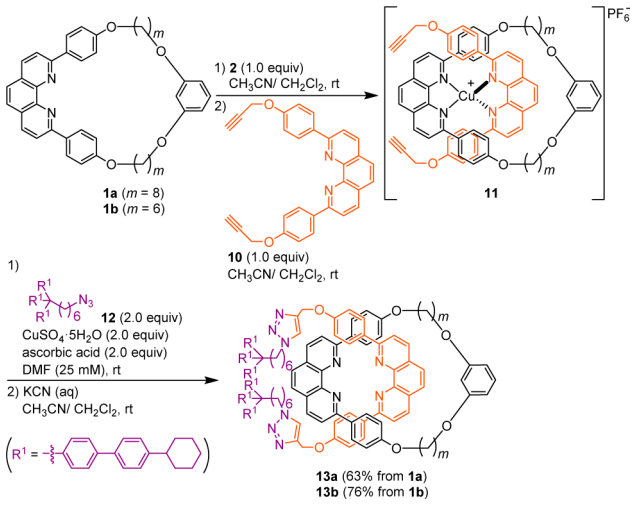
Synthesis of [2] and [3]Rotaxanes Using Huisgen Cycloaddition. In order to increase the yields of [3]rotaxane by suppressing the dissociation of the tetrahedral intermediate, we chose Cu-catalyzed azide−alkyne Huisgen cycloaddition (CuAAC), which usually proceed under milder conditions, as

Scheme 3. Synthesis of [3]Rotaxanes by Williamson Ether Synthesis



the end-capping reaction.[12e,g,k,l,o,16] We carried out the synthesis of [2]rotaxanes using Huisgen cycloaddition as the model reaction for the synthesis of [3]rotaxane. The results are summarized in Scheme 4. The tetrahedral Cu^{I} complex **11** was

Scheme 4. Synthesis of [2]Rotaxanes by Huisgen Cycloaddition



prepared *in situ* from **1**, **2**, and a bis(propargyl)phenanthroline derivative **10**.[17] The end-capping reaction using Huisgen cycloaddition was carried out between **11** and azide **12** in the presence of $CuSO_4{\cdot}5H_2O$ and ascorbic acid, which proceeded at room temperature. The crude product was treated with an excess of KCN, and [2]rotaxane **13** was isolated. When a 37-membered macrocyclic phenanthroline **1a** was used as the substrate, [2]rotaxane **13a** was obtained in 63% yield. The same reaction using a 33-membered macrocyclic phenanthroline **1b** also gave the corresponding [2]rotaxane **13b** in 76% yield.[18]

[3]Rotaxanes were also successfully synthesized by Huisgen cycloaddition. The results are summarized in Scheme 5. The tetrahedral Cu^{I} complex **14a** was prepared *in situ* from

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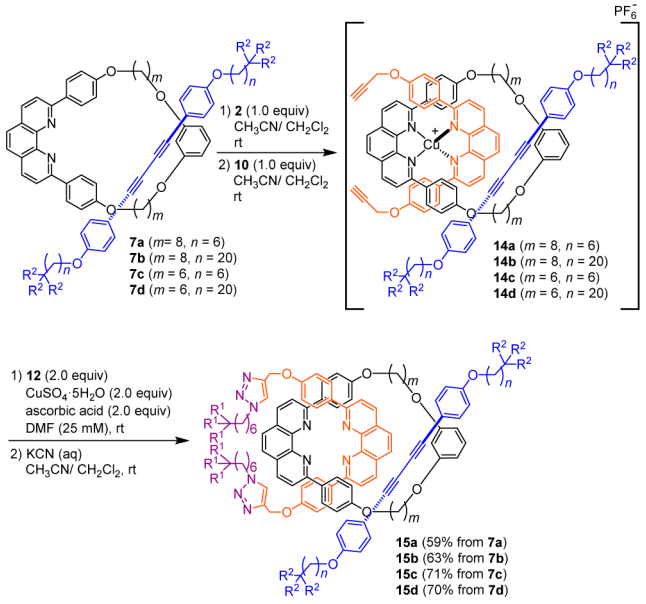
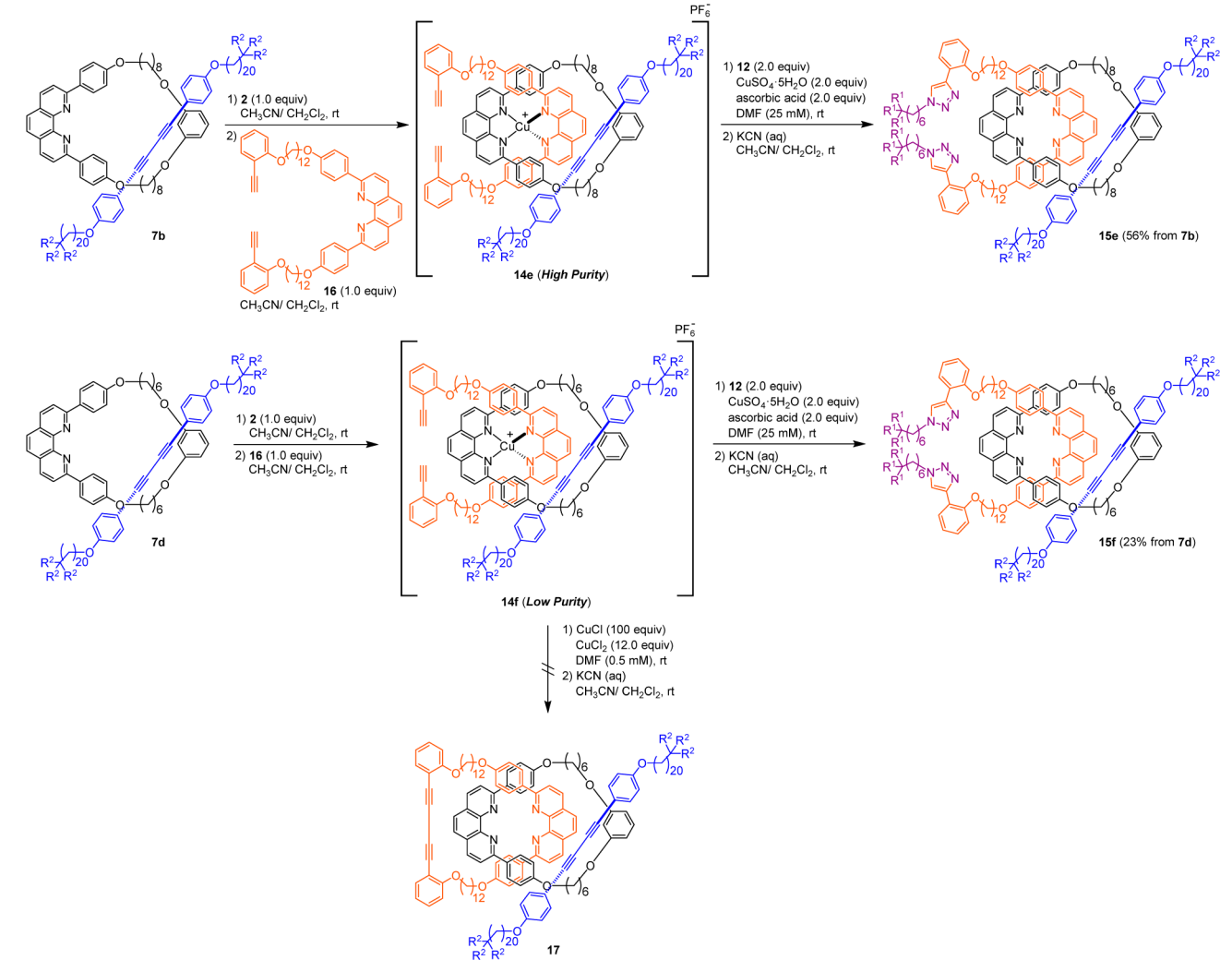
Scheme 5. Synthesis of [3]Rotaxanes by Huisgen Cycloaddition



[2]rotaxane **7a**, **2**, and **10**, and the bulky substituent was introduced. The removal of the Cu^{I} ion from the end-capped tetrahedral intermediate gave the corresponding [3]rotaxane **15a** in 59% yield. When [2]rotaxane **7b** was used as a substrate, [3]rotaxane **15b** was isolated in 63% yield. As we expected, the yields of [3]rotaxane with a 37-membered ring component increased by employing a milder end-capping reaction, and the yields of [3]rotaxanes **15a,b** were similar to that of [2]rotaxane **13a**. These results indicated that tetrahedral Cu^{I} complexes **14a,b** with a [2]rotaxane and an acyclic phenanthroline are stable under the reaction conditions, and the axle component did not interfere with the end-capping reaction (Huisgen cycloaddition). [2]Rotaxanes **7c,d** with a smaller ring component[4e,6,7m] could be converted to the tetrahedral Cu^{I} complexes **14c,d**,[19] and [3]rotaxanes **15c,d** were isolated in about 70% yields from **7c** and **7d**, respectively. It is noteworthy that rotacatenanes were not synthesized from **7c,d**,[6] whereas we succeeded in the synthesis of [3]rotaxanes from **7c,d**.

In order to understand the reason for the observed results, we studied the synthesis of [3]rotaxanes from **7b,d**, diyne **16**, and **12** (Scheme 6). We previously reported that the rotacatenane was synthesized by the reaction of **7b** and **16**. On the other hand, the attempted synthesis of the rotacatenane from **7d** and **16** failed: the low stability of the corresponding

Scheme 6. Synthesis of [3]Rotaxanes with a Longer Axle Component



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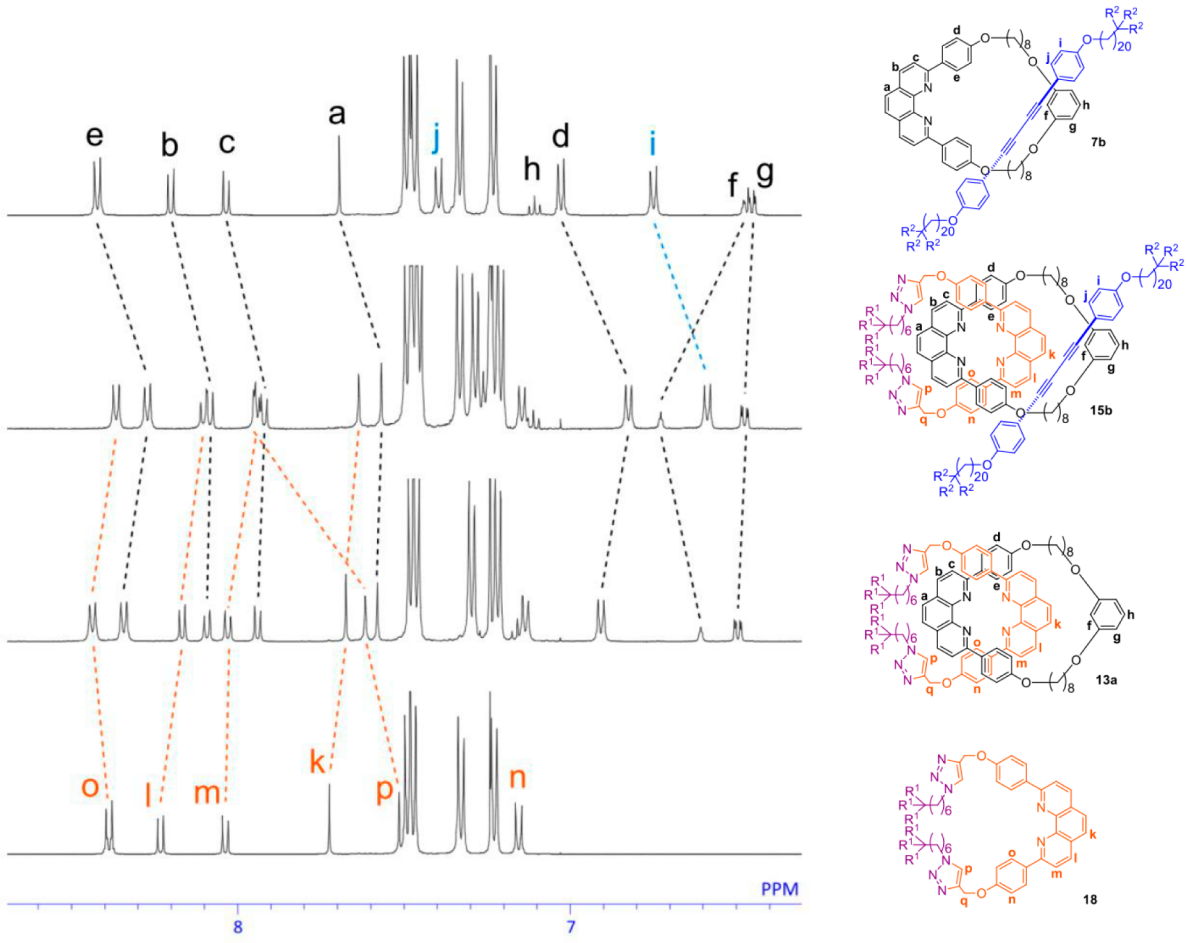

Figure 2. ^{1}H NMR spectra of [3]rotaxane **15b** and related compounds (500 MHz, $CDCl_3$).

tetrahedral Cu^I complex was assumed to be the reason for the unsuccessful result.[6] As we expected, the [3]rotaxane was synthesized by the reaction of **7b**, **16**, and **12** in 56% yield. Unexpectedly, the reaction of **7d**, **16**, and **12** also proceeded, and the corresponding [3]rotaxane was synthesized in lower yield (23%).[20] We assume that the yields of [3]rotaxane would be related to the stability of the tetrahedral Cu^I complex. In order to estimate the stability of the intermediate, we examined the ^{1}H NMR spectra of **14e** and **14f**. The ^{1}H NMR analyses indicated that formation of **14e** proceeded efficiently, reflecting the high stability of the complex. Meanwhile, the reaction of **7d**, **2**, and **16** resulted in the formation of **14f** and a mixture of byproducts, indicating the less stable nature of **14f**.[21] Since the [3]rotaxane **15f** was synthesized from a mixture of **14f** and other compounds, we re-examined the synthesis of the rotacatenane from **14f** in the presence of copper salts, but the rotacatenane **17** was not isolated.

The results we reported for the synthesis of [3]rotaxanes are complicated. It is possible, however, to explain the observed results by considering a couple of factors which would affect the stability of the tetrahedral Cu^I complexes. As we mentioned in the synthesis of rotacatenanes,[6] the size of the ring is a very important factor. When the size of the ring becomes small, the stability of the tetrahedral Cu^I complex would decrease due to the steric hindrance inside the cavity of the macrocyclic phenanthroline (e.g., **14e** vs **14f**). The second important factor is the structure of the acyclic phenanthroline ligand. When the size of the ligand is large, the tetrahedral Cu^I complex would be destabilized due to the steric hindrance outside the cavity of the macrocyclic phenanthroline (e.g., **14d** vs **14f**), that is, the steric hindrance between the [2]rotaxane moiety (the bulky blocking group of the axle component) and the acyclic phenanthroline ligand (ethynylphenyl group with a long methylene chain). The observed low yield of **15f** could be explained by considering these two factors. The third factor is the reaction conditions for the end-capping reaction. The decomposition of the tetrahedral Cu^I complex would be suppressed when the end-capping reaction was carried out under milder conditions. The observed low yields of **9a,b** compared to those of **15a,b** could be explained by considering the reaction conditions required for the end-capping reaction: a higher reaction temperature is required for the Williamson ether synthesis, which induces the decomposition of the tetrahedral Cu^I complex. The unsuccessful synthesis of a rotacatenane from **14f** could also be explained by considering the reaction conditions employed for the ring-closing reaction. In the presence of a large amount of copper salts, the formation of the rotacatenane could be inhibited since the decomposition of **14f** could proceed rapidly.

^{1}H NMR Spectra of [3]Rotaxanes. The ^{1}H NMR spectra of [3]rotaxane **15b**, [2]rotaxane **7b**, **13a**, and the unthreaded axle component **18** containing two triazole moieties are shown in Figure 2. As observed in many interlocked compounds we prepared, most of the signals of **7b**, **13a**, and **18** shifted upfield in [3]rotaxane **15b**. For example, the signals of protons of the *p*-alkoxyphenyl moiety ($H_{d,e}$), the phenanthroline moiety of **7b** ($H_{a\text{-}c}$), and the phenanthroline moiety of **13a** and **18** ($H_{k\text{-}m}$)

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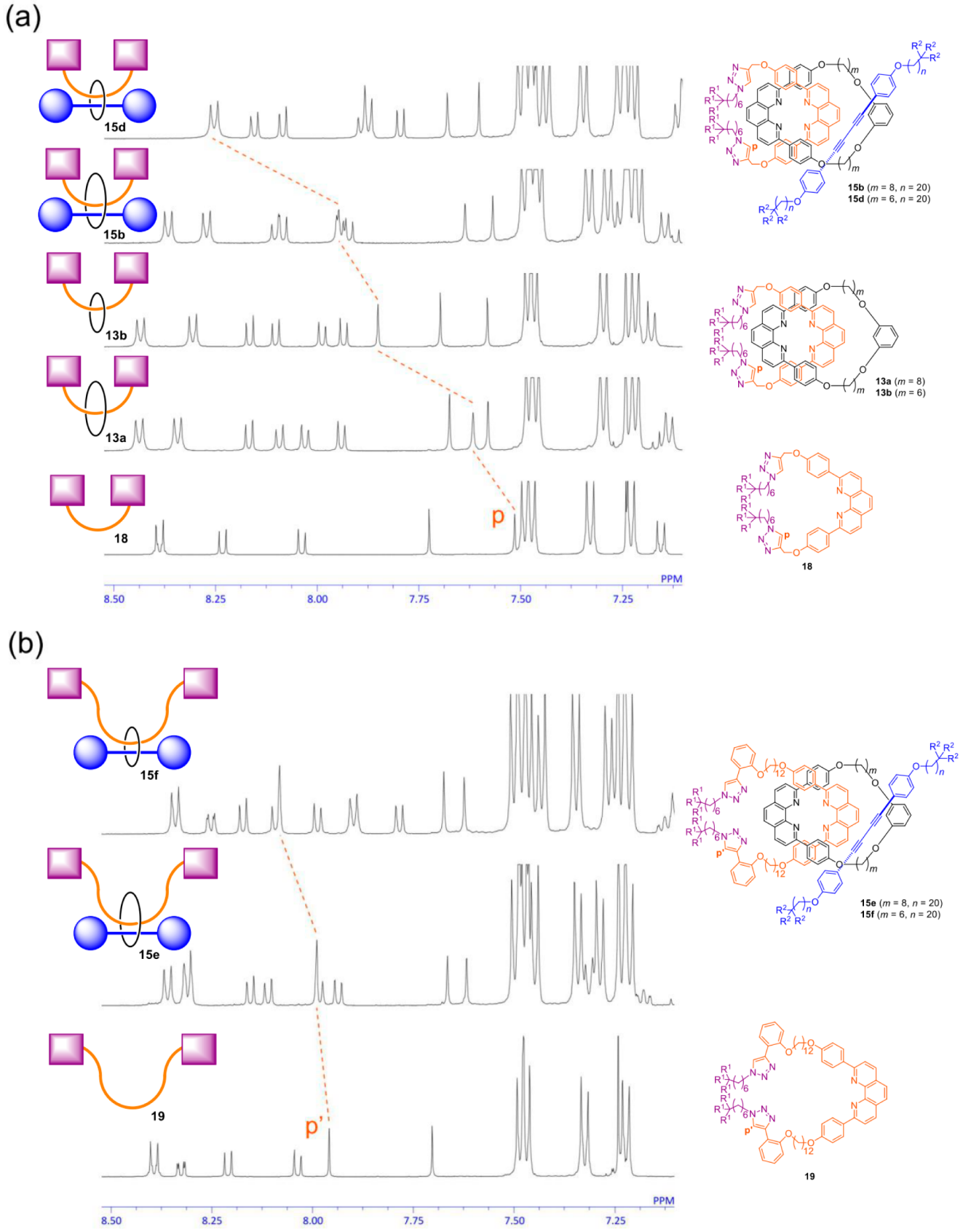

Figure 3. Chemical shift of the triazole proton (H_p or $H_{p'}$) in [2] and [3]rotaxanes (500 MHz, $CDCl_3$). (a) ^{1}H NMR spectra of [3]rotaxanes **15b,d**, [2]rotaxanes **13a,b**, and unthreaded axle component **18**. (b) ^{1}H NMR spectra of [3]rotaxanes **15e,f** and unthreaded axle component **19**.

shifted upfield in **15b**. In contrast, the signal of one proton of the resorcinol moiety of a macrocyclic phenanthroline (H_f) shifted downfield. The downfield shift of H_f was also observed in some interlocked compounds we synthesized.[4e,6,7a,m,9,12f]

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This downfield shift would reflect the presence of two linear components penetrating the macrocyclic ring. The signal of the protons of the triazole moiety (H_p) of **18** also significantly shifted downfield in **15b**.[22] The downfield shift of H_p, which was also observed in ^{1}H NMR spectra of [2]rotaxane **13a**, would be caused by the formation of the hydrogen bond between H_p and the nitrogen atom of the phenanthroline ring. The hydrogen bond between the hydrogen atom bound to a triazole ring and the nitrogen atom of a pyridine derivative was observed in some interlocked compounds.[7e,f,j,q,23]

To examine the relationship between the chemical shift of H_p and the structure of the rotaxane, we compared ^{1}H NMR spectra of rotaxanes (**13a**,**b** and **15b**,**d**), and the unthreaded axle component **18**, which are shown in Figure 3a. The chemical shift of H_p appeared downfield in [2]rotaxane **13b** compared to **13a**. The difference of these chemical shifts is in accordance with the results reported by Goldup and co-workers.[7q] They reported that the hydrogen bond of this type, which was a weak bond, intensified when the macrocycle was small. The downfield shift of H_p of [3]rotaxanes was more significant, and the chemical shift of H_p, which overlapped with a signal of H_o,[24] appeared at 8.35−8.20 ppm in [3]rotaxane **15d**. The axle components of [3]rotaxanes would be under a sterically hindered environment due to the presence of another axle component, and the chemical shift of H_p would be influenced. On the other hand, the difference of the chemical shift of $H_{p'}$ was less significant in [3]rotaxanes **15e**,**f** (Figure 3b). We assume that the increased flexibility of the axle components resulted in the reduced interaction between $H_{p'}$ and the phenanthroline moiety.

■ CONCLUSION

We developed a new synthetic method of [3]rotaxanes composed of two axle components and one cyclic component. To install two axle components in one ring, the combination of the catalytic threading reaction and metal-template approach was successfully employed. The stability of the tetrahedral Cu^I intermediate depended on the size of the ring moiety, the structure of the acyclic ligand, and the reaction conditions employed for the end-capping reaction, which influenced the yield of the [3]rotaxanes. By NMR analyses of the rotaxanes and related compounds, we disclosed that the strength of the hydrogen bond between the phenanthroline moiety could be affected by several factors such as the size of the ring component and the length of the axle component. The study would contribute to the understanding of the chemistry of complex interlocked compounds.

■ EXPERIMENTAL SECTION

Reagents were commercially available and used without further purification unless otherwise noted. Macrocyclic phenanthrolines (**1a**,**b**),[12f] 4,4′-(1,10-phenanthroline-2,9-diyl)diphenol (**3**),[11c] 4′,4‴,4′′′′-(7-iodoheptane-1,1,1-triyl)tris(4-cyclohexyl-1,1′-biphenyl) (**5**),[7m] [2]rotaxanes (**7a**−**d**),[4e,6,7m] 2,9-bis(4-(prop-2-yn-1-yloxy)-phenyl)-1,10-phenanthroline (**10**),[17a,b] and 2,9-bis(4-((12-(2-ethynyl-phenoxy)dodecyl)oxy)phenyl)-1,10-phenanthroline (**16**)[6] were prepared as reported. Chemical shifts were reported in delta units (δ) relative to chloroform-*d* (7.24 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR). Multiplicity is indicated by s (singlet), d (doublet), t (triplet) or m (multiplet). Coupling constants, *J*, are reported in Hz. A recycling preparative HPLC, equipped with high-resolution GPC column(s) (exclusion limit: 1000, 5000, or 30 000 MW), was used for the GPC separation (eluent: chloroform).

[2]Rotaxane (6).[7m] A mixture of macrocyclic phenanthroline **1a** (9.0 mg, 0.013 mmol) and $[Cu(CH_3CN)_4]PF_6$ (**2**) (4.8 mg, 0.013 mmol) in dry CH_2Cl_2 (1.0 mL) was stirred at room temperature for 20 min (mixture A). The reaction mixture was added to a suspension of **3** in dry CH_3CN (1.0 mL). A trace amount of mixture A in the flask was also added to the resulting mixture by using dry CH_2Cl_2 (1.0 mL). After stirring at room temperature for 1 h, the solvent was removed *in vacuo*. To the residue were added **5** (24 mg, 0.26 mmol), Cs_2CO_3 (17 mg, 0.52 mmol), and dry DMF (0.53 mL). The progress of the reaction was monitored by TLC, and the reaction mixture was stirred at 60 °C until **5** disappeared (2 days). The solvent was removed *in vacuo*, and CH_3CN (2.0 mL), CH_2Cl_2 (2.0 mL), H_2O (2.0 mL), and KCN (33 mg) were added to the residue. After stirring at room temperature for overnight, water and CH_2Cl_2 were added to the mixture. The organic layer and the aqueous layer were each separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography using hexane and CH_2Cl_2 (1:1 (v/v)) and GPC using $CHCl_3$ to afford **6** (18 mg, 6.6 μmol) in 51% yield as a pale yellow amorphous solid.

[3]Rotaxane (9a). A mixture of [2]rotaxane **7a** (34 mg, 0.013 mmol) and **2** (5.0 mg, 0.013 mmol) in dry CH_2Cl_2 (1.0 mL) was stirred at room temperature for 3 h (mixture A). The reaction mixture was added to a suspension of **3** (4.9 mg, 0.013 mmol) in dry CH_3CN (1.0 mL). A trace amount of mixture A in the flask was also added to the resulting mixture by using dry CH_2Cl_2 (2.0 mL). After stirring at room temperature for 1 h, the solvent was removed *in vacuo* and **5** (25 mg, 0.027 mmol), Cs_2CO_3 (18 mg, 0.054 mmol), and dry DMF (0.54 mL) were added to the residue. The progress of the reaction was monitored by TLC, and the reaction mixture was stirred at 60 °C until **5** disappeared (2 days). After the solvent was removed *in vacuo*, CH_3CN (2.0 mL), CH_2Cl_2 (2.0 mL), H_2O (2.0 mL), and KCN (33 mg) were added to the residue and the resulting mixture was stirred at room temperature for overnight. After water and CH_2Cl_2 were added to the mixture, the organic layer and the aqueous layer were each separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography using hexane and CH_2Cl_2 (1:1 (v/v)) and preparative thin-layer chromatography (PTLC) using CH_2Cl_2 and AcOEt (30:1 (v/v)) to afford **9a** (19 mg, 4.1 μmol) in 31% yield as a colorless amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (4H, d, *J* = 8.5 Hz), 8.28 (4H, d, *J* = 9.0 Hz), 8.10 (2H, d, *J* = 8.5 Hz), 7.98 (2H, d, *J* = 8.5 Hz), 7.93 (2H, d, *J* = 8.5 Hz), 7.83 (2H, d, *J* = 8.6 Hz), 7.62 (2H, s), 7.51 (2H, s), 7.49−7.38 (48H, m), 7.31−7.15 (52H, m), 7.05 (1H, t, *J* = 8.3 Hz), 6.97 (8H, d, *J* = 9.0 Hz), 6.70 (1H, t, *J* = 2.0 Hz), 6.49 (4H, d, *J* = 8.5 Hz), 6.43 (2H, dd, *J* = 8.5, 2.5 Hz), 3.93−3.78 (12H, m), 3.48 (4H, t, *J* = 6.5 Hz), 2.55−2.41 (20H, m), 1.94−1.59 (72H, m), 1.47−0.95 (104H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 160.5, 160.4, 159.5, 156.7, 156.2, 147.0, 146.9, 146.3, 146.2, 146.0, 138.34, 138.26, 138.2, 138.1, 136.5, 136.4, 134.0, 131.9, 131.5, 129.6, 129.5, 129.0, 128.8, 127.5, 127.3, 127.2, 127.1, 126.77, 126.75, 126.20, 126.17, 125.6, 125.3, 119.5, 119.1, 114.71, 114.67, 114.5, 113.4, 107.0, 101.3, 81.9, 73.7, 68.02, 67.97, 67.7, 55.9, 44.18, 44.16, 40.4, 40.3, 34.4, 30.5, 30.2, 29.81, 29.76, 29.70, 29.63, 29.56, 29.1, 26.9, 26.2, 26.1, 25.9, 25.74, 25.65; IR (KBr) 3025, 2924, 2850, 2140, 1904, 1602, 1588, 1496, 1447, 1247, 1173, 1005, 834, 813 cm^{-1}; HR-MS (MALDI-TOF) Calcd for $C_{330}H_{349}N_4O_8$ ($[M + H]^+$): 4495.7020. Found: 4495.6268.

[3]Rotaxane 9b. A mixture of [2]rotaxane **7b** (38 mg, 0.013 mmol) and **2** (4.8 mg, 0.013 mmol) in dry CH_2Cl_2 (1.5 mL) was stirred at room temperature for 4 h (mixture A). The reaction mixture was added to a suspension of **3** (4.7 mg, 0.013 mmol) in dry CH_3CN (1.0 mL). A trace amount of mixture A in the flask was also added to the resulting mixture by using dry CH_2Cl_2 (1.5 mL). After stirring at room temperature for 1 h, the solvent was removed *in vacuo* and **5** (24 mg, 0.026 mmol), Cs_2CO_3 (17 mg, 0.051 mmol), and dry DMF (0.52 mL) were added to the residue. The progress of the reaction was monitored by TLC, and the reaction mixture was stirred at 60 °C until **5** disappeared (2 days). After the solvent was removed *in vacuo*,

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CH_3CN (2.0 mL), CH_2Cl_2 (2.0 mL), H_2O (2.0 mL), and KCN (33 mg) were added to the residue and the mixture was stirred at room temperature for overnight. After water and CH_2Cl_2 were added to the mixture, the organic layer and the aqueous layer were each separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography using hexane and CH_2Cl_2 (1:1 (v/v)) and PTLC using CH_2Cl_2 and AcOEt (40:1 (v/v)) to afford **9b** (12 mg, 2.5 μmol) in 20% yield as a pale yellow amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (4H, d, J = 8.5 Hz), 8.31 (4H, d, J = 8.5 Hz), 8.13 (2H, d, J = 8.0 Hz), 8.09 (2H, d, J = 8.0 Hz), 7.96 (2H, d, J = 8.5 Hz), 7.91 (2H, d, J = 8.5 Hz), 7.65 (2H, s), 7.62 (2H, s), 7.50−7.42 (48H, m), 7.34 (12H, d, J = 8.0 Hz), 7.29−7.17 (40H, m), 7.07 (1H, t, J = 8.3 Hz), 6.99 (8H, d, J = 9.0 Hz), 6.70 (1H, s), 6.53 (4H, d, J = 9.0 Hz), 6.44 (2H, dd, J = 8.0, 2.5 Hz), 3.92−3.84 (12H, m), 3.56 (4H, t, J = 6.8 Hz), 2.63−2.55 (4H, m), 2.54−2.43 (16H, m), 1.96−1.60 (72H, m), 1.50−1.04 (160H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 160.44, 160.40, 159.6, 156.7, 156.3, 147.0, 146.9, 146.4, 146.3, 146.0, 138.32, 138.25, 138.19, 138.1, 136.5, 136.4, 134.0, 131.9, 131.5, 129.5, 129.0, 128.8, 127.5, 127.3, 127.14, 127.12, 126.8, 126.7, 126.21, 126.17, 125.6, 125.4, 119.5, 119.1, 114.7, 114.6, 114.4, 113.4, 107.0, 101.3, 81.8, 73.7, 68.00, 67.97, 67.94, 67.85, 56.0, 55.9, 44.2, 40.5, 40.4, 34.4, 30.5, 29.8, 29.74, 29.71, 29.67, 29.64, 29.57, 29.5, 29.4, 29.1, 26.9, 26.2, 26.1, 25.8, 25.7; IR (KBr) 3025, 2924, 2850, 2143, 1903, 1602, 1589, 1496, 1468, 1447, 1247, 1172, 1005, 834, 813 cm^{-1}; HR-MS (MALDI-TOF) Calcd for $C_{358}H_{405}N_4O_8$ ([M + H]$^+$): 4888.1402. Found: 4888.1459.

4′,4‴,4⁗-(7-Azidoheptane-1,1,1-triyl)tris(4-cyclohexyl-1,1′-biphenyl) (12). To a solution of **5** (0.46 g, 0.50 mmol) in DMF (1.0 mL) were added NaN_3 (39 mg, 0.60 mmol) and DMF (10 mL). After stirring for 14 h at 85 °C, the solvent was removed *in vacuo* and the residue was purified by flash column chromatography (silica gel) using hexane and CH_2Cl_2 (4:1 (v/v)). Further purification of the product was carried out by flash column chromatography (silica gel) using hexane and CH_2Cl_2 (4:1 (v/v)) to afford **12** (0.31 g, 0.37 mmol) in 74% yield as a white amorphous powder; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55−7.44 (12H, m), 7.34 (6H, d, J = 8.7 Hz), 7.28−7.20 (6H, m), 3.19 (2H, t, J = 6.9 Hz), 2.67−2.41 (5H, m), 1.96−1.67 (15H, m), 1.59−1.07 (23H, m); ^{13}C NMR (76 MHz, $CDCl_3$) δ 147.0, 146.2, 138.4, 138.1, 129.5, 127.1, 126.8, 126.2, 55.9, 51.4, 44.2, 40.3, 34.4, 29.9, 28.8, 26.9, 26.6, 26.1, 25.6; IR (KBr) 3024, 2923, 2849, 2092, 1495, 1447, 1261, 1003, 811, 526 cm^{-1}; Anal. Calcd for $C_{61}H_{69}N_3$: C, 86.78; H, 8.24; N, 4.98. Found: C, 86.68; H, 8.42; N, 4.92.

[2]Rotaxane (13a). To a solution of **2** (4.8 mg, 0.013 mmol) in dry CH_3CN (2.0 mL) was added the solution of **1a** (9.0 mg, 0.013 mmol) in dry CH_2Cl_2 (2.0 mL) and the mixture was stirred at room temperature for about 30 min. To the reaction mixture was added a solution of **10** (5.7 mg, 0.013 mmol) in dry CH_2Cl_2 (2.0 mL). After stirring at room temperature for 1 h, the solvent was removed *in vacuo*. To the residue were added **12** (22 mg, 0.026 mmol), $CuSO_4{\cdot}5H_2O$ (6.5 mg, 0.026 mmol), ascorbic acid (4.6 mg, 0.026 mmol), and dry DMF (0.52 mL). The progress of the reaction was monitored by TLC, and the reaction mixture was stirred at room temperature until **12** disappeared (1 day). After the solvent was removed *in vacuo*, CH_2Cl_2 (2.0 mL), CH_3CN (2.0 mL), H_2O (2.0 mL), and KCN (40 mg) were added to the residue and the purple solution was stirred at room temperature until the color of the mixture turned into yellow (overnight). CH_2Cl_2 was added to the solution, and the aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography using CH_2Cl_2 and PTLC using CH_2Cl_2 and AcOEt (80/1 (v/v)) to afford **13a** (23 mg, 8.3 μmol) in 63% yield as a pale yellow amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (4H, d, J = 8.5 Hz), 8.34 (4H, d, J = 8.5 Hz), 8.17 (2H, d, J = 8.6 Hz), 8.09 (2H, d, J = 8.6 Hz), 8.03 (2H, d, J = 8.6 Hz), 7.94 (2H, d, J = 8.6 Hz), 7.67 (2H, s), 7.62 (2H, s), 7.58 (2H, s), 7.50−7.44 (24H, m), 7.30 (12H, d, J = 8.6 Hz), 7.22 (12H, d, J = 8.0 Hz), 7.18−7.11 (5H, m), 6.91 (4H, d, J = 8.6 Hz), 6.61 (1H, s), 6.49 (2H, dd, J = 8.6, 2.3 Hz), 5.05 (4H, s), 3.89 (8H, t, J = 6.6 Hz), 3.71 (4H, t, J = 6.9 Hz), 2.55−2.43 (10H, m), 1.91−1.77 (24H, m), 1.76−1.63 (10H, m), 1.60−1.09 (58H, m), 1.08−0.99 (4H, m), 0.98−0.89 (4H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 159.5, 156.5, 156.0, 147.1, 146.1, 146.0, 143.5, 138.4, 138.1, 136.8, 132.4, 131.6, 129.9, 129.5, 128.9, 127.5, 127.4, 127.2, 126.8, 126.2, 125.62, 125.57, 123.0, 119.4, 119.2, 115.0, 114.7, 106.8, 101.2, 67.9, 67.8, 62.0, 55.9, 50.0, 44.2, 40.3, 34.4, 30.2, 29.8, 29.3, 29.24, 29.17, 26.9, 26.3, 26.1, 25.9, 25.5; IR (KBr) 3025, 2924, 2850, 1603, 1588, 1575, 1492, 1447, 1249, 1174, 1004, 837, 814 cm^{-1}; HR-MS (ESI) Calcd for $C_{198}H_{210}N_{10}O_6$ ([M + 2H]$^{2+}$): 1411. 82119. Found: 1411. 81991.

[2]Rotaxane (13b). To a solution of **2** (4.8 mg, 0.013 mmol) in dry CH_3CN (2.0 mL) was added the solution of **1b** (8.3 mg, 0.013 mmol) in dry CH_2Cl_2 (2.0 mL), and the mixture was stirred at room temperature for 30 min. To the reaction mixture was added a solution of **10** (5.7 mg, 0.013 mmol) in dry CH_2Cl_2 (2.0 mL). After stirring at room temperature for 1 h, the solvent was removed *in vacuo*. To the residue were added **12** (22 mg, 0.026 mmol), $CuSO_4{\cdot}5H_2O$ (6.5 mg, 0.026 mmol), ascorbic acid (4.6 mg, 0.026 mmol), and dry DMF (0.52 mL). The progress of the reaction was monitored by TLC, and the reaction mixture was stirred at room temperature until **12** disappeared (1 day). After the solvent was removed *in vacuo*, CH_2Cl_2 (2.0 mL), CH_3CN (2.0 mL), H_2O (2.0 mL), and KCN (40 mg) were added to the residue and the purple solution was stirred at room temperature until the color of the mixture turned into yellow (overnight). CH_2Cl_2 was added to the solution, and the aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by PTLC using CH_2Cl_2 and AcOEt (20/1 (v/v)) to afford **13b** (27 mg, 9.8 μmol) in 76% yield as a pale yellow amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (4H, d, J = 9.5 Hz), 8.31 (4H, d, J = 8.5 Hz), 8.17 (2H, d, J = 8.5 Hz), 8.10 (2H, d, J = 8.5 Hz), 7.99 (2H, d, J = 8.5 Hz), 7.93 (2H, d, J = 8.5 Hz), 7.85 (2H, s), 7.70 (2H, s), 7.58 (2H, s), 7.52−7.42 (24H, m), 7.30 (12H, d, J = 8.5 Hz), 7.25−7.10 (17H, m), 6.81 (4H, d, J = 9.0 Hz), 6.70 (1H, t, J = 2.3 Hz), 6.52 (2H, dd, J = 8.5, 2.5 Hz), 5.10 (4H, s), 3.93 (4H, t, J = 6.0 Hz), 3.84 (4H, t, J = 7.5 Hz), 3.71 (4H, t, J = 7.3 Hz), 2.55−2.42 (10H, m), 1.92−1.77 (24H, m), 1.77−1.68 (10H, m), 1.68−1.60 (4H, m), 1.50−1.15 (42H, m), 1.15−0.97 (8H, m), 0.92−0.79 (4H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 160.3, 159.6, 156.6, 156.0, 147.1, 146.1, 146.0, 145.9, 143.6, 138.4, 138.1, 136.8, 132.4, 131.6, 130.0, 129.5, 129.0, 128.9, 127.5, 127.4, 127.2, 126.8, 126.3, 125.6, 123.1, 119.5, 119.2, 115.0, 114.7, 106.8, 101.3, 67.8, 67.7, 62.2, 55.9, 50.0, 44.2, 40.3, 34.4, 30.2, 29.8, 29.5, 28.9, 26.9, 26.3, 26.1, 25.8, 25.6, 25.5; IR (KBr) 3025, 2925, 2851, 1603, 1588, 1494, 1448, 1249, 1174, 1005, 837, 814 cm^{-1}; HR-MS (ESI) Calcd for $C_{194}H_{202}N_{10}O_6$ ([M + 2H]$^{2+}$): 1383.78989. Found: 1383.78987.

[3]Rotaxane (15a). To a solution of **2** (7.8 mg, 0.021 mmol) in dry CH_3CN (1.2 mL) was added the solution of [2]rotaxane **7a** (53 mg, 0.021 mmol) in dry CH_2Cl_2 (2.5 mL), and the mixture was stirred at room temperature for 3 h. To the reaction mixture was added a solution of **10** (9.2 mg, 0.021 mmol) in dry CH_2Cl_2 (2.5 mL). After stirring at room temperature for 1 h, the solvent was removed *in vacuo*. To the residue were added **12** (35 mg, 0.042 mmol), $CuSO_4{\cdot}5H_2O$ (10 mg, 0.042 mmol), ascorbic acid (7.4 mg, 0.042 mmol), and dry DMF (0.84 mL). The progress of the reaction was monitored by TLC, and the reaction mixture was stirred at room temperature until **12** disappeared (2 days). After the solvent was removed *in vacuo*, CH_2Cl_2 (2.5 mL), CH_3CN (2.5 mL), H_2O (2.5 mL), and KCN (60 mg) were added to the residue. The purple solution was stirred at room temperature until the mixture turned into a yellow suspension (overnight). After water and CH_2Cl_2 were added to the suspension, the organic layer and the aqueous layer were each separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography using CH_2Cl_2 and GPC using $CHCl_3$ to afford **15a** (57 mg, 0.012 mmol) in 59% yield as a pale yellow amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (4H, d, J = 8.5 Hz), 8.28 (4H, d, J = 9.0 Hz), 8.06 (2H, d, J = 8.0 Hz), 8.01 (2H, d, J = 8.0 Hz), 7.92−7.87 (6H, m), 7.55 (4H, s), 7.47−7.43 (48H, m), 7.30−7.28 (24H, m), 7.23−7.21 (28H, m),

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7.14−7.08 (5H, m), 6.81 (4H, d, J = 8.5 Hz), 6.75 (1H, t, J = 2.5 Hz), 6.55 (4H, d, J = 9.0 Hz), 6.47 (2H, dd, J = 8.0, 2.0 Hz), 5.05 (4H, s), 3.95 (4H, t, J = 6.5 Hz), 3.78 (4H, t, J = 7.5 Hz), 3.72 (4H, t, J = 7.0 Hz), 3.57 (4H, t, J = 6.5 Hz), 2.55−2.40 (20H, m), 1.88−1.70 (64H, m), 1.64−1.52 (4H, m), 1.52−0.93 (104H, m), 0.87−0.74 (4H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160. 6, 160.4, 159.6, 159.5, 156.8, 156.0, 147.03, 147.01, 146.2, 146.14, 146.09, 145.8, 143.6, 138.4, 138.3, 138.10, 138.06, 136.7, 136.6, 134.0, 132.3, 131.4, 129.6, 129.5, 129.0, 127.5, 127.3, 127.2, 126.8, 126.24, 126.22, 125.6, 125.5, 123.1, 119.7, 119.1, 114.9, 114.6, 114.5, 113.3, 107.1, 101.0, 81.9, 73.7, 68.0, 67.9, 67.8, 62.3, 55.9, 55.8, 49.9, 44.2, 40.33, 40.29, 34.4, 30.3, 30.2, 29.82, 29.80, 29.76, 29.7, 29.4, 29.1, 26.9, 26.3, 26.2, 26.1, 26.0, 25.8, 25.7, 25.6; IR (KBr) 3025, 2923, 2850, 2656, 2140, 1904, 1603, 1591, 1496, 1465, 1448, 1247, 1173, 1005, 835, 813 cm^{-1}; HR-MS (MALDI-TOF) Calcd for $C_{336}H_{355}N_{10}O_8$ ([M + H]$^+$): 4657.7674. Found: 4657.6961.

[3]Rotaxane (15b). To a solution of **2** (6.3 mg, 0.017 mmol) in dry CH_3CN (1.0 mL) was added a solution of [2]rotaxane **7b** (50 mg, 0.017 mmol) in dry CH_2Cl_2 (2.0 mL), and the mixture was stirred at room temperature for 3.5 h. To the reaction mixture was added a solution of **10** (7.5 mg, 0.017 mmol) in dry CH_2Cl_2 (2.0 mL). After stirring at room temperature for 1 h, the solvent was removed *in vacuo*. To the residue were added **12** (29 mg, 0.034 mmol), $CuSO_4{\cdot}5H_2O$ (8.5 mg, 0.034 mmol), ascorbic acid (6.0 mg, 0.034 mmol), and dry DMF (0.68 mL). The progress of the reaction was monitored by TLC, and the reaction mixture was stirred at room temperature until **12** disappeared (1 day). After the solvent was removed *in vacuo*, CH_2Cl_2 (2.0 mL), CH_3CN (2.0 mL), H_2O (2.0 mL), and KCN (60 mg) were added to the residue. The purple solution was stirred at room temperature until the mixture turned into a yellow suspension (overnight). After water and CH_2Cl_2 were added to the reaction mixture, the organic layer and the aqueous layer were each separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography using CH_2Cl_2 and GPC using $CHCl_3$ to afford **15b** (54 mg, 0.011 mmol) in 63% yield as a pale yellow amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (4H, d, J = 8.5 Hz), 8.27 (4H, d, J = 9.0 Hz), 8.13−8.06 (4H, m), 7.97−7.90 (6H, m), 7.64 (2H, s), 7.57 (2H, s), 7.53−7.42 (48H, m), 7.33 (12H, d, J = 9.0 Hz), 7.31−7.19 (40H, m), 7.17−7.09 (5H, m), 6.82 (4H, d, J = 9.0 Hz), 6.73 (1H, s), 6.59 (4H, d, J = 9.0 Hz), 6.47 (2H, dd, J = 8.0, 2.0 Hz), 5.06 (4H, s), 3.96 (4H, t, J = 6.8 Hz), 3.81 (4H, t, J = 7.0 Hz), 3.75 (4H, t, J = 6.8 Hz), 3.64 (4H, t, J = 6.8 Hz), 2.62−2.55 (4H, m), 2.54−2.42 (16H, m), 1.93−1.68 (64H, m), 1.67−0.95 (164H, m), 0.90−0.80 (4H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 160.4, 159.7, 159.6, 156.9, 156.1, 147.03, 146.99, 146.4, 146.2, 146.1, 145.9, 143.6, 138.4, 138.3, 138.2, 138.1, 136.7, 136.6, 134.0, 132.3, 131.5, 129.6, 129.5, 129.03, 128.99, 127.5, 127.4, 127.2, 127.1, 126.78, 126.75, 126.24, 126.21, 125.6, 125.5, 123.2, 119.8, 119.2, 114.9, 114.6, 114.5, 113.3, 107.1, 101.1, 81.9, 73.6, 68.0, 67.93, 67.91, 62.3, 56.0, 55.9, 49.9, 44.2, 40.5, 40.3, 34.4, 30.5, 30.3, 29.8, 29.74, 29.72, 29.67, 29.65, 29.6, 29.53, 29.46, 29.4, 29.1, 26.9, 26.4, 26.2, 26.13, 26.07, 25.9, 25.7, 25.6; IR (KBr) 3025, 2924, 2850, 2666, 2140, 1904, 1602, 1588, 1495, 1467, 1447, 1247, 1173, 1005, 834, 813 cm^{-1}; HR-MS (MALDI-TOF) Calcd for $C_{364}H_{411}N_{10}O_8$ ([M + H]$^+$): 5050.2056. Found: 5050.2071.

[3]Rotaxane (15c). To a solution of **2** (7.7 mg, 0.021 mmol) in dry CH_3CN (1.2 mL) was added a solution of [2]rotaxane **7c** (51 mg, 0.021 mmol) in dry CH_2Cl_2 (2.5 mL), and the mixture was stirred at room temperature for 3 h. To the reaction mixture was added a solution of **10** (9.1 mg, 0.021 mmol) in dry CH_2Cl_2 (2.5 mL). After stirring at room temperature for 1 h, the solvent was removed *in vacuo*. To the residue were added **12** (35 mg, 0.041 mmol), $CuSO_4{\cdot}5H_2O$ (10 mg, 0.041 mmol), ascorbic acid (7.3 mg, 0.041 mmol), and dry DMF (0.83 mL). The progress of the reaction was monitored by TLC, and the reaction mixture was stirred at room temperature until **12** disappeared (1 day). After the solvent was removed *in vacuo*, CH_2Cl_2 (2.5 mL), CH_3CN (2.5 mL), H_2O (2.5 mL), and KCN (60 mg) were added to the residue. The dark red solution was stirred at room temperature until the mixture turned into a yellow suspension (overnight). After water and CH_2Cl_2 were added to the reaction mixture, the organic layer and the aqueous layer were each separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography using CH_2Cl_2 and GPC using $CHCl_3$ to afford **15c** (68 mg, 0.015 mmol) in 71% yield as a pale yellow amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31−8.15 (6H, m), 8.11−8.03 (4H, m), 7.87 (4H, d, J = 8.5 Hz), 7.82 (2H, d, J = 8.5 Hz), 7.79 (2H, d, J = 9.0 Hz), 7.60 (2H, s), 7.57 (2H, s), 7.52−7.40 (48H, m), 7.30 (12H, d, J = 8.0 Hz), 7.28−7.18 (36H, m), 7.12−7.05 (9H, m), 6.94 (1H, t, J = 2.3 Hz), 6.81 (4H, d, J = 8.5 Hz), 6.50−6.44 (6H, m), 5.13 (4H, s), 4.05 (4H, t, J = 6.8 Hz), 3.94 (4H, t, J = 7.0 Hz), 3.88−3.79 (4H, br), 3.54 (4H, t, J = 6.5 Hz), 2.57−2.44 (16H, m), 2.44−2.36 (4H, m), 1.93−1.77 (52H, m), 1.77−1.68 (16H, m), 1.65−0.92 (96H, m), 0.91−0.80 (4H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.7, 159.9, 159.6, 159.5, 158.2, 156.2, 147.02, 147.00, 146.5, 146.24, 146.17, 145.9, 143.2, 138.4, 138.11, 138.06, 136.6, 136.5, 133.9, 132.4, 132.2, 129.5, 129.4, 129.3, 128.9, 127.6, 127.3, 127.1, 126.8, 126.7, 126.2, 125.8, 125.5, 123.9, 121.1, 119.2, 115.0, 114.7, 114.3, 113.3, 107.4, 101.7, 82.5, 74.4, 68.3, 67.8, 67.7, 62.4, 55.90, 55.85, 49.9, 44.2, 40.4, 40.3, 34.4, 30.2, 30.1, 29.9, 29.8, 29.4, 29.1, 26.9, 26.4, 26.1, 26.0, 25.8, 25.7, 25.6; IR (ATR) 3027, 2921, 2848, 1907, 1601, 1493, 1446, 1244, 1171, 1004, 832, 810, 778, 745, 526 cm^{-1}; HR-MS (MALDI-TOF) Calcd for $C_{332}H_{347}N_{10}O_8$ ([M + H]$^+$): 4601.7048. Found: 4601.7211.

[3]Rotaxane (15d). To a solution of **2** (7.5 mg, 0.020 mmol) in dry CH_3CN (1.2 mL) was added a solution of [2]rotaxane **7d** (57 mg, 0.020 mmol) in dry CH_2Cl_2 (2.4 mL), and the mixture was stirred at room temperature for 3 h. To the reaction mixture was added a solution of **10** (8.8 mg, 0.020 mmol) in dry CH_2Cl_2 (2.4 mL). After stirring at room temperature for 1 h, the solvent was removed *in vacuo*. To the residue were added **12** (34 mg, 0.04 mmol), $CuSO_4{\cdot}5H_2O$ (10 mg, 0.040 mmol), ascorbic acid (7.0 mg, 0.040 mmol), and dry DMF (0.80 mL). The progress of the reaction was monitored by TLC, and the reaction mixture was stirred at room temperature until **12** disappeared (2 days). After the solvent was removed *in vacuo*, CH_2Cl_2 (2.4 mL), CH_3CN (2.4 mL), H_2O (2.4 mL), and KCN (60 mg) were added to the residue. The purple solution was stirred at room temperature until the mixture turned into a yellow suspension (overnight). After water and CH_2Cl_2 were added to the reaction mixture, the organic layer and the aqueous layer were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography using CH_2Cl_2 and GPC using $CHCl_3$ to afford **15d** (70 mg, 0.014 mmol) in 70% yield as a pale yellow amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35−8.19 (6H, m), 8.15 (2H, d, J = 8.5 Hz), 8.08 (2H, d, J = 8.0 Hz), 7.92−7.85 (6H, m), 7.79 (2H, d, J = 8.5 Hz), 7.68 (2H, s), 7.60 (2H, s), 7.53−7.41 (48H, m), 7.34 (12H, d, J = 8.5 Hz), 7.28−7.19 (36H, m), 7.14−7.07 (9H, m), 6.96 (1H, s), 6.83 (4H, d, J = 8.5 Hz), 6.52−6.45 (6H, m), 5.13 (4H, s), 4.07 (4H, t, J = 7.0 Hz), 3.96 (4H, t, J = 7.0 Hz), 3.91−3.82 (4H, br), 3.60 (4H, t, J = 6.5 Hz), 2.64−2.56 (4H, m), 2.56−2.45 (12H, m), 2.45−2.37 (4H, m), 1.97−1.68 (68H, m), 1.62−1.10 (144H, m), 1.10−1.02 (4H, m), 1.02−0.94 (4H, m), 0.93−0.83 (4H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.7, 159.9, 159.7, 159.5, 158.2, 156.2, 147.03, 146.99, 146.5, 146.4, 146.2, 146.0, 143.2, 138.4, 138.2, 138.1, 136.6, 136.5, 133.9, 132.5, 132.2, 129.6, 129.50, 129.45, 129.4, 128.9, 127.6, 127.4, 127.2, 127.1, 126.8, 126.7, 126.2, 125.8, 125.5, 123.9, 121.2, 119.2, 115.0, 114.7, 114.3, 113.3, 107.5, 101.6, 82.5, 74.4, 68.3, 67.83, 67.77, 62.4, 56.0, 55.9, 49.9, 44.2, 40.5, 40.3, 34.4, 30.5, 30.1, 29.9, 29.8, 29.73, 29.70, 29.64, 29.57, 29.50, 29.40, 29.37, 29.1, 26.9, 26.4, 26.1, 26.0, 25.9, 25.7, 25.6; IR (ATR) 3029, 2921, 2849, 1907, 1602, 1493, 1466, 1446, 1244, 1171, 1004, 832, 810, 778, 747, 525 cm^{-1}; HR-MS (MALDI-TOF) Calcd for $C_{360}H_{403}N_{10}O_8$ ([M + H]$^+$): 4994.1430. Found: 4994.1110.

[3]Rotaxane (15e). To a solution of **2** (7.0 mg, 0.019 mmol) in dry CH_3CN (1.1 mL) was added a solution of [2]rotaxane **7b** (55 mg, 0.019 mmol) in dry CH_2Cl_2 (2.3 mL), and the mixture was stirred at room temperature for 3 h. To the reaction mixture was added a solution of **16** (18 mg, 0.019 mmol) in dry CH_2Cl_2 (2.3 mL). After

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stirring at room temperature for 1 h, the solvent was removed *in vacuo*. To the residue were added **12** (32 mg, 0.038 mmol), $CuSO_4·5H_2O$ (9.4 mg, 0.038 mmol), ascorbic acid (6.6 mg, 0.038 mmol), and dry DMF (0.75 mL). The progress of the reaction was monitored by TLC, and the reaction mixture was stirred at room temperature until **12** disappeared (1 day). After the solvent was removed *in vacuo*, CH_2Cl_2 (2.3 mL), CH_3CN (2.3 mL), H_2O (2.3 mL), and KCN (54 mg) were added to the residue. The purple solution was stirred at room temperature until the mixture turned into a yellow suspension (overnight). After water and CH_2Cl_2 were added to the reaction mixture, the organic layer and the aqueous layer were each separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexane/CH_2Cl_2 1:1 (v/v) and CH_2Cl_2) and PTLC using CH_2Cl_2 and AcOEt (80:1 (v/v)) to afford **15e** (59 mg, 0.011 mmol) in 56% yield as a colorless amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (4H, d, J = 8.5 Hz), 8.33−8.28 (6H, m), 8.15 (2H, d, J = 8.6 Hz), 8.11 (2H, d, J = 8.0 Hz), 8.01−7.96 (4H, m), 7.94 (2H, d, J = 8.0 Hz), 7.66 (2H, s), 7.62 (2H, s), 7.53−7.42 (48H, m), 7.37−7.26 (28H, m), 7.26−7.15 (26H, m), 7.09 (1H, t, J = 8.3 Hz), 7.04−6.94 (10H, m), 6.82 (2H, d, J = 9.0 Hz), 6.66 (1H, s), 6.60 (4H, d, J = 8.5 Hz), 6.46 (2H, dd, J = 8.0, 2.5 Hz), 4.19 (4H, t, J = 7.3 Hz), 3.97−3.82 (16H, m), 3.67 (4H, t, J = 6.8 Hz), 2.64−2.56 (4H, m), 2.55−2.44 (16H, m), 1.95−1.66 (80H, m), 1.62−1.51 (4H, m), 1.48−1.03 (188H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 160.44, 160.36, 159.7, 156.6, 156.3, 155.0, 147.0, 146.4, 146.3, 146.2, 146.0, 143.0, 138.4, 138.3, 138.2, 138.1, 136.6, 134.0, 132.0, 131.8, 129.6, 129.5, 129.0, 128.9, 128.6, 127.54, 127.52, 127.4, 127.1, 126.77, 126.75, 126.2, 125.6, 125.5, 123.0, 120.7, 119.6, 119.5, 119.2, 114.7, 114.6, 114.5, 113.4, 111.5, 106.9, 101.3, 81.8, 73.7, 68.2, 68.01, 67.99, 67.97, 67.9, 56.0, 55.9, 50.0, 44.2, 40.5, 40.3, 34.4, 30.5, 30.4, 29.9, 29.8, 29.73, 29.70, 29.66, 29.63, 29.60, 29.57, 29.55, 29.52, 29.48, 29.39, 29.37, 29.3, 29.1, 26.9, 26.4, 26.21, 26.18, 26.13, 26.10, 25.9, 25.7, 25.6; IR (ATR) 3026, 2921, 2849, 2664, 1907, 1602, 1489, 1469, 1447, 1245, 1172, 1004, 833, 812, 750, 528 cm^{-1}; HR-MS (MALDI-TOF) Calcd for $C_{398}H_{463}N_{10}O_{10}$ ([M + H]$^+$): 5542.6023. Found: 5542.6216.

[3]Rotaxane (15f). To a solution of **2** (7.5 mg, 0.020 mmol) in dry CH_3CN (1.2 mL) was added a solution of [2]rotaxane **7d** (57 mg, 0.020 mmol) in dry CH_2Cl_2 (2.4 mL), and the mixture was stirred at room temperature for 3 h. To the reaction mixture was added a solution of **16** (19 mg, 0.020 mmol) in dry CH_2Cl_2 (2.4 mL). After stirring at room temperature for 1 h, the solvent was removed *in vacuo*. To the residue were added **12** (34 mg, 0.040 mmol), $CuSO_4·5H_2O$ (10 mg, 0.040 mmol), ascorbic acid (7.0 mg, 0.040 mmol), and dry DMF (0.80 mL). The progress of the reaction was monitored by TLC, and the reaction mixture was stirred at room temperature until **12** disappeared (1 day). After the solvent was removed *in vacuo*, CH_2Cl_2 (2.4 mL), CH_3CN (2.4 mL), H_2O (2.4 mL), and KCN (57 mg) were added to the residue. The dark red solution was stirred at room temperature until the mixture turned into a yellow suspension (overnight). After water and CH_2Cl_2 were added to the reaction mixture, the organic layer and the aqueous layer were each separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (hexane/CH_2Cl_2 2:1 (v/v), CH_2Cl_2 and CH_2Cl_2/AcOEt 30:1 (v/v)) to afford **15f** (25 mg, 4.6 μmol) in 23% yield as a pale yellow amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (4H, d, J = 8.5 Hz), 8.25 (2H, dd, J = 7.8, 1.8 Hz), 8.17 (2H, d, J = 8.5 Hz), 8.11−8.06 (4H, m), 7.99 (2H, d, J = 8.5 Hz), 7.90 (4H, d, J = 9.0 Hz), 7.78 (2H, d, J = 8.5 Hz), 7.67 (2H, s), 7.62 (2H, s), 7.53−7.40 (48H, m), 7.35 (12H, d, J = 9.0 Hz), 7.30−7.18 (36H, m), 7.15−7.05 (7H, m), 7.03 (4H, d, J = 8.5 Hz), 6.98−6.85 (7H, m), 6.81 (2H, d, J = 8.0 Hz), 6.52−6.43 (6H, m), 4.13 (4H, t, J = 7.0 Hz), 4.08−4.00 (8H, m), 3.97 (4H, t, J = 6.8 Hz), 3.85 (4H, t, J = 6.8 Hz), 3.63 (4H, t, J = 6.5 Hz), 2.66−2.56 (4H, m), 2.56−2.42 (16H, m), 1.98−1.64 (80H, m), 1.63−1.48 (4H, m), 1.48−1.00 (180H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 160.5, 159.7, 159.5, 158.2, 156.3, 155.0, 147.0, 146.7, 146.4, 146.2, 146.0, 142.9, 138.3, 138.2, 138.1, 136.6, 136.3, 133.8, 133.2, 131.8, 129.6, 129.5, 129.4, 128.9, 128.4, 127.54, 127.51, 127.4, 127.1, 126.8, 126.7, 126.2, 125.8, 125.5, 123.2, 121.1, 120.5, 119.6, 119.2, 114.8, 114.7, 114.3, 113.3, 111.5, 107.3, 101.6, 82.3, 74.3, 68.24, 68.20, 68.0, 67.9, 67.6, 56.0, 55.9, 50.0, 44.2, 40.5, 40.3, 34.4, 30.4, 30.3, 30.0, 29.9, 29.71, 29.68, 29.62, 29.57, 29.5, 29.4, 29.3, 29.2, 29.1, 26.9, 26.5, 26.13, 26.05, 25.93, 25.89, 25.7, 25.6; IR (ATR) 3027, 2921, 2849, 1602, 1489, 1471, 1447, 1243, 1171, 1004, 832, 810, 750, 530 cm^{-1}; HR-MS (MALDI-TOF) Calcd for $C_{394}H_{455}N_{10}O_{10}$ ([M + H]$^+$): 5486.5397. Found: 5486.5500.

18. Colorless amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (4H, d, J = 9.5 Hz), 8.23 (2H, d, J = 8.6 Hz), 8.04 (2H, d, J = 8.6 Hz), 7.72 (2H, s), 7.51 (2H, s), 7.51−7.44 (24H, m), 7.33 (12H, d, J = 8.6 Hz), 7.26−7.21 (12H, m), 7.15 (4H, d, J = 9.0 Hz), 5.28 (4H, s), 4.26 (4H, t, J = 7.5 Hz), 2.61−2.54 (4H, m), 2.54−2.45 (6H, m), 1.91−1.77 (28H, m), 1.76−1.68 (6H, m), 1.47−1.09 (42H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 156.2, 147.0, 146.1, 146.0, 143.9, 138.4, 138.0, 136.8, 132.6, 129.5, 129.0, 127.5, 127.1, 126.7, 126.2, 125.6, 122.5, 119.3, 115.1, 62.1, 55.9, 50.3, 44.1, 40.2, 34.4, 30.1, 29.7, 26.8, 26.3, 26.1, 25.4; IR (KBr) 3025, 2923, 2849, 1604, 1495, 1447, 1245, 1175, 1005, 837, 813 cm^{-1}; HR-MS (ESI) Calcd for $C_{152}H_{160}N_8O_2$ ([M + 2H]$^{2+}$): 1064.63226. Found: 1064.63322.

19. Colorless amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (4H, d, J = 9.0 Hz), 8.33 (2H, dd, J = 8.3, 1.8 Hz), 8.21 (2H, d, J = 8.5 Hz), 8.04 (2H, d, J = 8.5 Hz), 7.96 (2H, s), 7.70 (2H, s), 7.51−7.44 (24H, m), 7.32 (12H, d, J = 8.5 Hz), 7.27−7.19 (14H, m), 7.08−7.00 (6H, m), 6.90 (2H, d, J = 8.0 Hz), 4.31 (4H, t, J = 7.3 Hz), 4.04−3.97 (8H, m), 2.63−2.55 (4H, m), 2.55−2.44 (6H, m), 1.92−1.69 (42H, m), 1.50−1.09 (74H, m); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4, 156.3, 155.0, 147.0, 146.1, 146.0, 143.1, 138.4, 138.1, 136.7, 131.9, 129.5, 128.9, 128.7, 127.6, 127.5, 127.1, 126.8, 126.2, 125.5, 122.8, 120.8, 119.5, 119.2, 114.7, 111.5, 68.1, 68.0, 55.9, 50.1, 44.2, 40.3, 34.4, 30.3, 29.8, 29.62, 29.58, 29.55, 29.4, 29.34, 29.26, 26.9, 26.4, 26.2, 26.1, 26.0, 25.5; IR (ATR) 3025, 2921, 2849, 1902, 1603, 1587, 1489, 1466, 1446, 1244, 1173, 1115, 1067, 1041, 1004, 836, 811, 750, 563, 525, 486, 475, 446 cm^{-1}; HR-MS (ESI) Calcd for $C_{186}H_{212}N_8O_4$ ([M + 2H]$^{2+}$): 1310.83103. Found: 1310.83498.

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra (^{1}H, ^{13}C, COSY, HSQC, HMBC) for new compounds, MALDI-TOF MS spectra (observed and simulated) of **9a** and **15a**, and comparison of the ^{1}H NMR spectra of **9a** and related compounds (pdf file). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01120.

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Notes

The authors declare no competing financial interest.

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(13) A reviewer suggested using the term "active-metal template approach", which was proposed by Leigh, to describe this approach. We highly appreciate Leigh's outstanding contribution in this field. We prefer, however, to use a more concise term such as "catalytic threading approach", or, to be more accurate, "metal-mediated threading approach", to describe the synthetic approach. The importance of the role of the metal as the "catalyst" or the mediator for the bond-forming process is emphasized in these terms.

(14) [2]Rotaxane **6** was obtained in 54% yield from **1a** when the concentration of **4** was 50 mM (see ref 7m). This reaction was carried out to compare the efficiency of the end-capping reactions under similar conditions (concentration).

(15) Decomposition of **5** and tetrahedral Cu^{I} complex was observed during the monitoring of the end-capping reaction. Demetalation of **8** (or monoalkylated **8**) might proceed due to the presence of Cs_2CO_3 and hot DMF before the formation of the [3]rotaxane **9**−Cu^{I} complex.

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(18) Unthreaded linear component **18** with two triazole moieties was also isolated (see the Supporting Information).

(19) In ^{1}H NMR spectra of the crude product, we confirmed that **14c**,**d** were the major products.

(20) Unthreaded linear component **19** with two triazole moieties was also isolated (see the Supporting Information).

(21) The dissociation of **14e** did not proceed during the purification by silica gel column chromatography, and **14e** was isolated in high yield. However, the decomposition of **14f** was observed during the attempted purification (see ref 6). The results indicated that **14f** is less stable than **14e**. In the synthesis of **14f**, a byproduct, which was assumed as another copper complex composed of two **16**, was observed during the monitoring of the reaction (TLC and ^{1}H NMR analysis). As a reviewer mentioned, the observed results might be attributed to another factor such as the relative activation barrier for the formation of **14e**,**f**. At present, we cannot discuss this possibility since we have no data related to the activation energy of the process. The details concerning the formation of **14e**,**f** are under investigation. We are grateful for the reviewer's kind suggestions.

(22) In the HMBC spectra of **13a**, the signal of H_q, which was observed at 5.05 ppm in ^{1}H NMR spectra, correlated with a quaternary carbon atom of a triazole moiety of which the signal was observed at 143.53 ppm in ^{13}C NMR spectra. Another singlet signal, which appeared at 7.62 ppm in ^{1}H NMR spectra, also correlated with the same carbon atom, and the signal was identified with that of H_p. The assignment of H_p of **13b**, **15a**, or **15b** was achieved similarly. The signal of H_p of **18** was identified by the comparison of ^{1}H NMR spectra of **18** and another phenanthroline derivative.

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(24) The signals of H_p and H_o were separated in a ^{1}H NMR analysis which was performed in DMSO-d_6/$CDCl_3$ (see the Supporting Information).

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