Ph. D. Thesis

（博士論文）

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

（銅を用いたカップリング反応と金属テンプレート法を組み合わせた ロタカテナンと[3]ロタキサンの合成）

Research Advisor Prof. Shinichi Saito

Tokyo University of Science
Graduate School of Chemical Sciences and Technology
Department of Chemical Sciences and Technology

Ryuto Hayashi（林 竜人）
### Abbreviation

<table>
<thead>
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<tbody>
<tr>
<td>Ac</td>
<td>acetyl</td>
</tr>
<tr>
<td>COSY</td>
<td>correlation spectroscopy</td>
</tr>
<tr>
<td>DEAD</td>
<td>diethyl azodicarboxylate</td>
</tr>
<tr>
<td>DMF</td>
<td>(N,N)-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>equiv</td>
<td>equivalent</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>HMBC</td>
<td>hetero-nuclear multiple-bond connectivity</td>
</tr>
<tr>
<td>HSQC</td>
<td>hetero-nuclear single quantum coherence</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>NOESY</td>
<td>nuclear Overhauser effect correlated spectroscopy</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>rt</td>
<td>room temperature</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilyl</td>
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Chapter 1

Introduction

Rotaxanes and catenanes are representative interlocked compounds composed of several components, and these compounds are generally named as \([n]\)rotaxane or \([n]\)catenane when the number of the components is \(n\). For example, a \([2]\)catenane is composed of two ring components. A \([2]\)rotaxane is composed of one axle component and one ring component (Figure 1-1a). It is expected that rotaxanes and catenanes are promising candidates for the construction of nanomaterials such as a molecular motor and a molecular switch due to the high mobilities of the components such as shuttling and rotation. Because of this, these compounds have been great interest for decades, which induced the development of many synthetic methods of \([2]\)rotaxane and \([2]\)catenane utilizing template synthesis, self-assembly, or transition metal-catalyzed coupling reaction.\(^1\)

![Figure 1-1. Structures of interlocked compounds.](image)
With the remarkable progress in the synthesis of [2]rotaxanes and [2]catenanes, the chemistry of complex interlocked compounds composed of three or more components have been studied.\textsuperscript{2-8} The structures of the interlocked compounds with three components are depicted in Figure 1-1b. [3]Catenane is composed of three ring components.\textsuperscript{2,3} There are two types of [3]rotaxane: a [3]rotaxane (type 1. 2) is composed of one axle component and two ring components,\textsuperscript{4} while a [3]rotaxane (type 2. 1) is composed of two axle components and one axle component.\textsuperscript{5} Rotacatenane incorporate the structural feature of both [2]rotaxane and [2]catenane into a single molecule.\textsuperscript{7} [3]Catenane and [3]rotaxane (type 1. 2) were synthesized by many groups. However, [3]rotaxane (type 2. 1) and rotacatenane are very rare. In the synthesis of a rotacatenane and a [3]rotaxane (type 2. 1), the ring component with larger size than required for a [2]rotaxane would be necessary in order to aggregate two components in its cavity. However, the dissociation of the components would proceed when the ring component is large, and the stoppers of the axle component(s) with larger size would be required for stabilizing the interlocked structure. The difficulty to synthesize the rotacatenane and the [3]rotaxane (type 2. 1) would be attributed to these factors depending on the structural feature.
To synthesize the rotacatenane and the [3]rotaxane (type 2.1), I made use of the characteristics of transition metal. Transition metals have often been used for the synthesis of rotaxanes and catenanes (Scheme 1-1). For example, Leigh and co-workers developed the synthetic method of a [2]rotaxane using transition metal-mediated bond-forming reaction in 2006.\(^9\) In their approach, Huisgen cycloaddition proceeded in the cavity of macrocyclic pyridine-Cu complex, and metal-free [2]rotaxane was obtained in good yield after the removal of the Cu ion. Subsequently, Saito and co-workers reported the synthesis of [2]rotaxanes and [2]catenanes by the oxidative coupling of alkyne using macrocyclic 1,10-phenanthroline-Cu complex (Scheme 1-1a),\(^10\) and the catalytic threading approach (known as also active-metal template approach) turned out to be an efficient strategy for the synthesis of [2]rotaxanes and [2]catenanes.\(^11\) The synthesis of interlocked
compounds using the macrocyclic phenanthroline was reported by Sauvage and co-workers in 1980s, which was achieved by using Cu(I) ion as the template (Scheme 1-1b). Thus, the reaction of phenanthroline derivatives with Cu(I) salt gave a stable tetrahedral Cu(I) complex, and the cyclization of the acyclic ligand was carried out. The corresponding [2]catenane was yielded by removing the Cu(I) ion. The metal-template approach was applied to the synthesis of a [2]rotaxane by Gibson and co-workers.

In Chapters 2-4, I described the efficient synthesis of rotacatenanes, sequential rotacatenane isomers, and [3]rotaxanes by the combination of the catalytic threading approach and the metal-template approach as shown in Schemes 1-2, 1-3, and 1-4. NMR spectra of the isolated compounds were discussed. In each Chapter, the detailed background and target of the study were described.
Synthesis of Rotacatenanes by the Combination of Copper-Mediated Coupling Reaction and Metal-Template Approach (Chapter 2)

As the first section of my thesis, I described the synthesis of rotacatenanes by the combination of copper-mediated coupling reaction and metal-template method in Chapter 2.\(^1\) The synthetic method of rotacatenane is shown in Scheme 1-2.

Scheme 1-2. A Strategy for the Synthesis of Rotacatenane

Thus, [2]rotaxanes were prepared by the oxidative coupling of alkyne using macrocyclic phenanthroline-Cu complex. The installation of another ring component in the [2]rotaxane was achieved by using Cu(I) ion as template, the metal-free rotacatenane was synthesized by the removal of the Cu(I) ion. In this approach, the size of the macrocyclic phenanthroline turned out to be a very important factor for the synthesis of rotacatenane.
Sequence-Selective Synthesis of Rotacatenane Isomers (Chapter 3)

When the number of the components which constitute the interlocked compound increase, an issue of the sequential isomer will arise: depending on the connectivity of the components, two or more compounds would exist. In the next part, I described the sequence-selective synthesis of rotacatenane isomers (Scheme 1-3) which was achieved by the application of the strategy for the synthesis of rotacatenanes we developed.

Scheme 1-3. A Strategy for the Synthesis of Rotacatenane Isomers by the Combination of (a) Catalytic Threading Approach and (b) Metal-Template Approach
Thus, two [2]rotaxanes with different phenanthroline moieties were synthesized by the oxidative coupling of alkyne with bulky blocking group, which was proceeded in the cavity of the macrocyclic phenanthroline-Cu complex. The metal template method was used to install another cyclic component: the tetrahedral Cu(I) complex, which was composed of a [2]rotaxane and an acyclic phenanthroline derivative, was synthesized and the cyclization of the phenanthroline derivative gave the rotacatenane. The sequential isomers of rotacatenane were distinguished by $^1$H and $^{13}$C NMR spectroscopy.

Synthesis of [3]Rotaxanes by the Combination of Copper-Mediated Coupling Reaction and Metal-Template Approach (Chapter 4)

In the final part is described the synthesis of [3]rotaxanes (type 2. 1) by the combination of copper-mediated coupling reaction and metal-template approach. The synthetic method of [3]rotaxanes is shown in Scheme 1-4.\textsuperscript{19}
Thus, [2]rotaxanes were prepared by the oxidative coupling of alkyne promoted by macrocyclic phenanthroline-Cu 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.

I believe that the results and the perspectives in this thesis will contribute to further development of the synthetic method of complex interlocked compounds.
References for Chapter 1


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4. For recent examples of the synthesis of [3]rotaxanes (type 1. 2) with one axle component and
two ring components, see: (a) Neal, E. A.; Goldup, S. M. Chem. Sci. 2015, 6, 2398-2404. (b)


Chapter 2

Synthesis of Rotacatenanes by the Combination of Copper-Mediated Coupling Reaction and Metal-Template Approach

2.1 Introduction

Rotacatenane is a molecule which incorporates the structural features of rotaxanes and catenanes into a single molecule.\textsuperscript{1,2} The synthesis of this intriguing molecule was reported for the first time by Stoddart and co-workers in 1999.\textsuperscript{2} Their synthetic strategy, which is shown in Scheme 2-1, was based on the use of the strong non-bonding interaction between the cationic bipyridinium ion and the electron-rich aromatic ring, and the structure as well as the switching properties of these rotacatenanes were studied thoroughly. No other studies related to rotacatenanes have been reported to date, however, and the synthesis as well as the properties of the rotacatenanes remain to be studied in depth.\textsuperscript{3}
The recent development of a new strategy for the synthesis of interlocked compounds utilizing the catalytic activity of the macrocyclic metal complexes\textsuperscript{4,11} prompted us to design a new strategy for the synthesis of rotacatenanes (Scheme 2-2). Thus, the oxidative dimerization of an alkyne with a large blocking group would be mediated by a macrocyclic phenanthroline-CuI complex, and the [2]rotaxane would be synthesized efficiently since the reaction would proceed inside the ring.\textsuperscript{4c-i} The installation of another ring component would be achieved by the template method, which was originally reported by Sauvage and co-workers.\textsuperscript{1c,g} In our synthetic approach, the coordinating
ability of the macrocyclic phenanthroline was used for both the synthesis of [2]rotaxanes (by the formation of the catalytically active Cu complex) and the installation of another ring component (by the template effect). Herein, we report the synthesis of rotacatenanes based on the abovementioned strategy.

Scheme 2-2. A New Strategy for the Synthesis of Rotacatenanes
2.2 Results and Discussion

The synthesis of [2]rotaxanes was achieved by the reaction of macrocyclic phenanthroline-CuI complexes with terminal alkynes with a bulky blocking group. The oxidative dimerization (Glaser coupling) of 2 was examined in the presence of a macrocyclic phenanthroline-CuI complex (1), I₂, and K₂CO₃.⁴₆,⁵ The mixture was heated in xylene at 130 °C for 48 h, and then treated with aqueous ammonia⁶ to remove the Cu ion. Since this reaction proceeded inside the ring, the formation of [2]rotaxane (3) would be preferred. Two phenanthroline-CuI complexes (1a and 1b) with different ring size were chosen as the starting materials, and they were reacted with terminal alkynes with different chain lengths (2a-c). The results are summarized in Table 2-1.

The reaction of a smaller phenanthroline-CuI complex 1a (m = 6) with 2a, an alkyne with a shorter methylene bridge (n = 6) and a tris(biphenyl)methyl group (blocking group), gave the corresponding [2]rotaxane in high yield (entry 1).⁴₆ The reaction of alkyne 2b which possessed a longer methylene bridge (n = 20)⁷ and a bulkier blocking group (tris(4-cyclohexylbiphenyl)methyl group)⁸ with 1a also gave the corresponding [2]rotaxane 3b in 76% yield (entry 2). On the other hand, the yield of 3 decreased when a larger phenanthroline-CuI complex 1b (m = 8) was used as the substrate (entries 3 and 4).⁹ The observed lower yields of 3c and 3d might be due to the progress of the dissociation of the components (deslipping reaction) during the synthesis of 3c and 3d. Since the reaction was carried out at 130 °C, the deslipping reaction might proceed after the formation of a [2]rotaxane-CuI complex.¹⁰ Alternatively, the efficiency of the threading reaction might have
decreased due to the increased flexibility of the macrocyclic ring.

Table 2-1. Preparation of [2]Rotaxanes by Cu-Mediated Oxidative Coupling of Alkyne

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cul complex</th>
<th>Alkyne</th>
<th>Product</th>
<th>Yield$^a$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a (33-membered ring)</td>
<td>2a</td>
<td>3a</td>
<td>72</td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>2b</td>
<td>3b</td>
<td>76</td>
</tr>
<tr>
<td>3</td>
<td>1b (37-membered ring)</td>
<td>2c</td>
<td>3c</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>1b</td>
<td>2b</td>
<td>3d</td>
<td>43</td>
</tr>
</tbody>
</table>

$a$) Isolated yield from 1.
Next, we investigated the synthesis of [2]catenanes from macrocyclic phenanthrolines by the template method (Scheme 2-3). The tetrahedral Cu(I) complex 7 was synthesized by the reaction of macrocyclic phenanthroline 4, [Cu(CH$_3$CN)$_4$]PF$_6$ (5), and 6. Complex 7 turned out to be stable enough to be purified by silica gel column chromatography. The cyclization of 7 proceeded in the presence of an excess of CuCl and CuCl$_2$. [2]Catenane 8a ($m = 6$) was isolated in 38% yield by the removal of the Cu(I) ion from the complex. Similarly, a larger [2]catenane 8b ($m = 8$) as isolated in 46% yield.
Table 2-2. Synthesis of Rotacatenanes from [2]Rotaxanes and 6

<table>
<thead>
<tr>
<th>Entry</th>
<th>[2]Rotaxane</th>
<th>m</th>
<th>n</th>
<th>Product</th>
<th>Yield(^a) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3a</td>
<td>6</td>
<td>6</td>
<td>10a</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>3b</td>
<td>6</td>
<td>20</td>
<td>10b</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>3c</td>
<td>8</td>
<td>6</td>
<td>10c</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>3d</td>
<td>8</td>
<td>20</td>
<td>10d</td>
<td>26</td>
</tr>
</tbody>
</table>

\(^a\) Isolated yield from 3.

With these successful results in hand, we studied the synthesis of rotacatenanes by the combination of two methodologies (Table 2-2). Tetrahedral Cu(I) complexes 9 were synthesized
by the reaction of 3, 5, and 6. Next, the cyclization of 9 was conducted in the presence of an excess of CuCl and CuCl₂. Finally, the Cu(I) ion was removed to isolate the rotacatenane 10. The initial attempts for the synthesis of the rotacatenane from 3a were unsuccessful (entries 1 and 2). During the monitoring of the reaction, we noticed that the tetrahedral Cu(I) complexes (9a and 9b) were unstable: the attempted isolation of 9a and 9b failed, and the decomposition of 9a and 9b was observed.

In contrast, we succeeded in the synthesis of rotacatenanes when [2]rotaxanes with a larger ring component were used as substrates. Thus, the tetrahedral Cu(I) complex 9c, which was synthesized from 3c, 5, and 6, was stable and could be purified by silica gel column chromatography. The oxidative cyclization-demetalation proceeded smoothly, and the rotacatenane 10c was isolated in 33% yield (entry 3). The tetrahedral Cu(I) complex 9d, which incorporates a longer axle, was also stable, and the corresponding rotacatenane was isolated in 26% yield (entry 4). These results indicated that the size of the ring of the [2]rotaxane is very important for the synthesis of the rotacatenane. A possible explanation for these results is summarized in Figure 2-1. When the size of the ring is small, the tetrahedral complex would be destabilized because of the steric interaction between the two fragments. Meanwhile, [2]rotaxanes with a larger ring (3c and 3d) could incorporate the phenanthroline ligand 6 into the cavity and the tetrahedral complexes are stable.
Figure 2-1. Relationship between the size of macrocyclic phenanthroline and the stability of tetrahedral Cu(I) complexes

The structure of the rotacatenane was confirmed by mass spectroscopy as well as NMR spectroscopy. The $^1$H NMR spectra of 3d, 10d, and 11 (prepared by the cyclization of 6) are shown in Figure 2-2. As a result of the interaction between the components, the spectrum of 10d was different from those of 3d or 11. For example, the signal of $p$-alkoxyphenyl moieties and arylalkyne moieties of 11 (H$_{1k}$) and $p$-alkoxyphenyl moieties of 3d (H$_e$) shifted upfield in 10d. The upfield shifts of other signals were also observed. However, the signal of H$_a$, which is one of the hydrogen atoms of the resorcinol moiety of the macrocyclic phenanthroline unit of 3d, appeared at 6.47 ppm, while that of 10d shifted downfield and appeared at 6.73 ppm.$^{13}$
Figure 2-2. $^1$H NMR spectra of 11 (synthesized by the cyclization of 6, see Supporting Information), rotacatenane 10d and [2]rotaxane 3d (500 MHz, CDCl$_3$).
2.3 Conclusion

In summary, we synthesized rotacatenanes by the combination of the Cu-mediated threading reaction and the template method. The macrocyclic phenanthroline framework was initially used as the ligand for the Cu-mediated oxidative coupling reaction, and then used again as the template for the installation of the cyclic fragment. The study provided a new approach for the synthesis of complex interlocked compounds.
References for Chapter 2

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3. In Contrast, the synthesis of [3]rotaxanes has been studied extensively. See: (a) Anderson, S.;  


5309-5314.


8. It was necessary to introduce this larger blocking group to prevent the facile deslipping reactions when 1b was used as the ring component. See: Saito, S.; Nakazono, K.; Takahashi, E. *J. Org. Chem.* **2006**, *71*, 7477-7480.

9. In these reactions, the dimer of the alkyne with a bulky blocking group (2b or 2c) was isolated in *ca.* 30% yield when 1b was used as the substrate.

10. The rate of the deslipping reaction of 3c was studied previously. We assume that the stability of 3d would be comparable to that of 3c. See ref 5.

12. Some signals which were similar to those of 9c and 9d were detected in the NMR spectra of the mixture, indicating the formation of 9a and 9b.

13. The 1H NMR spectra of compound 12 (prepared by the dimerization of 2b), rotacatenane 10d and [2]catenane 8b were also compared, and again the shifts of many signals were observed. See Supporting Information.
Chapter 3

Sequence-Selective Synthesis of Rotacatenane Isomers

3.1 Introduction

![Diagram of interlocked compounds]

Figure 3-1. Sequential isomers of [3]rotaxane (type 1. 2), rotacatenane and [3]catenane.

In the chemistry of interlocked compounds with three or more components, a unique issue related to the connectivity of the components would arise (Figure 3-1). For example, two isomers of [3]rotaxane (type 1. 2) would exist when the symmetry of the axle component is low and the translocation of the two different ring component is not possible. Leigh and co-workers reported the selective synthesis of [3]rotaxanes (type 1. 2) with two different ring components, which are
the sequential isomers due to the difference in the array of two ring components. The number of reported examples related to the selective synthesis of two or more sequential isomers of interlocked compounds, however, is quite limited: only one sequential isomer was synthesized in most studies. To the best of our knowledge, no example has been reported for the selective synthesis of two or more sequential isomers of rotacatenanes or [3]catenanes. Accordingly, the chemistry related to the sequential isomerism of interlocked compounds, which is a very interesting phenomenon, remains to be studied in depth.

The first synthesis of rotacatenane was reported by Stoddart and co-workers in 1999, and the study related to the application of the rotacatenane to a molecular device was subsequently carried out. The strong non-bonding interaction between the bipyridinium ion and the aromatic ring was utilized to synthesize rotacatenanes. We recently reported the synthesis of rotacatenanes, which was based on a different strategy. A [2]rotaxane, which was prepared by oxidative coupling of alkyne utilizing the catalytic activity of macrocyclic phenanthroline-CuI complex, was reacted with a Cu(I) salt and an acyclic phenanthroline ligand. The cyclization of the tetrahedral Cu(I) complex and the subsequent removal of Cu(I) ion resulted in the synthesis of the rotacatenane. The combination of the Cu-mediated threading reaction and the metal-template method turned out to be an efficient strategy for the synthesis of rotacatenane.
We envisioned that the sequence selective synthesis of rotacatenane isomers could be realized by applying the synthetic strategy we established (Scheme 3-1). Two different macrocyclic phenanthrolines $1a$ and $1b$ are designed, and [2]rotaxanes $2a$ and $2b$ would be prepared by the oxidative coupling of alkyne using $1a$-$CuI$ and $1b$-$CuI$, respectively (Scheme 3-1a). Rotacatenane $3a$ would be synthesized by the installation of the different ring component in $2a$ using Cu(I) ion as template (Scheme 3-1b). Another rotacatenane $3b$ would be also synthesized from $2b$. If we would design two ring compounds which would be used as the ligand in Scheme 3-1a and install...
the same cyclic structure in the late-stage cyclization (Scheme 3-1b), it is possible to install two
different ring components in a different sequence to a rotacatenane. Two rotacatenanes (3a and 3b)
are sequential isomers: the structure of the three components of 3a and 3b are identical, and the
isomerism was induced by the difference in the connectivity of the components. In this chapter, we
report the sequence-selective synthesis of the isomeric rotacatenanes.
3.2 Results and Discussion

Preparation of macrocyclic phenanthrolines and [2]rotaxanes. As the precursor of the rotacatenanes, we designed and synthesized two macrocyclic phenanthrolines. The results are shown in Scheme 3-2.

Mitsunobu reaction of 2-((trimethylsilyl)ethynyl)phenol (4) with 6-chloro-1-hexanol (5a) gave 6a, and 6a was reacted with a phenanthroline derivative (7) under basic condition to yield 8a. The cyclization of 8a was carried out in the presence of CuCl and CuCl$_2$. The macrocyclic phenanthroline 1a was isolated in 55% yield when the reaction was carried out under highly diluted condition: the initial concentration of 1a was set to 0.5 mM. A macrocyclic phenanthroline 1b, which is composed of an oxygen-tethered alkylene group, was also synthesized from 4 in 4 steps.
These phenanthroline derivatives are useful precursors for the synthesis of the isomers of rotacatenane: the ring size of the macrocycles would be suitable for the synthesis of rotacatenanes, and the acyclic derivatives (8a and 8b) would be employed as the precursor for the late-stage cyclization.


The synthesis of [2]rotaxanes was described in Scheme 3-3. The macrocyclic phenanthroline-Cu complex 1a-CuI was synthesized by the reaction of 1a with Cul, and 1a-CuI was reacted with an alkyne (9) in the presence of K2CO3 and I2 at 80 °C for 3 days. The crude product was treated with aqueous ammonia to remove the Cu ion from the [2]rotaxane-Cu complex. The formation of the [2]rotaxane was sluggish when the reaction was carried out in xylene or THF/toluene. We assume that the low solubility of 1a-CuI in these solvents

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was responsible for the observed slow rate of the reaction. We found that 1a-CuI has better solubility in 1,1,2,2-tetrachloroethane. The reaction of 1a-CuI with 9 proceeded smoothly in 1,1,2,2-tetrachloroethane and the [2]rotaxane 2a was isolated in 43% yield. [2]Rotaxane 2b was also synthesized under similar reaction conditions: the reaction of 1b-CuI with 9 proceeded in 1,2-dichloroethane, and the corresponding [2]rotaxane was isolated in 46% yield.

**Synthesis of rotacatenane isomers.** Having [2]rotaxanes 2a and 2b in hand, rotacatenane isomers were synthesized by the metal-template method. The results are summarized in Scheme 3-4.

**Scheme 3-4. Synthesis of Rotacatenane Isomers**

[2]Rotaxane 2a was reacted with [Cu(CH3CN)4]PF6 and 8b, and the formation of a tetrahedral Cu(I) complex 10a was observed. The crude product was purified by silica gel column
chromatography, and 10a was isolated as stable red solid in 79% yield. As we expected, the tetrahedral complex 10a could be employed as a stable substrate, which does not undergo facile dissociation, under the conditions required for the further transformation. The cyclization of the acyclic phenanthroline moiety of 10a was carried out in the presence of CuCl and CuCl2 at room temperature under highly diluted conditions: the initial concentration of 10a was set to 0.5 mM in DMF. After 3 days, the crude product was treated with an excess amount of KCN to remove the Cu(I) ion from the rotacatenane-Cu(I) complex. The rotacatenane 3a was isolated in 62% yield from 10a. The synthesis of another rotacatenane (3b), which is a sequential isomer of 3a, was also examined. Compound 2b was converted to the tetrahedral Cu(I) complex 10b under similar reaction conditions described for the synthesis of 10a. An acyclic phenanthroline 8a was introduced as the ligand, and 10b was isolated in 70% yield. The cyclization of 10b proceeded smoothly, and the rotacatenane isomer 3b was isolated in 71% yield from 10b after the removal of Cu(I) ion.

**Comparison of the NMR spectra of [2]rotaxane and rotacatenanes.** The structure of the [2]rotaxane and the rotacatenane isomers were examined by NMR spectroscopy. The 1H NMR spectra of [2]rotaxane 2a, the macrocyclic phenanthroline 1a and the unthreaded axle component 11 are shown in Figure 3-2. As expected, the NMR spectrum of [2]rotaxane 2a was different from those of 1a and 11. For example, the signal of the protons of the phenanthroline moieties of 1a (H_{A-C}) and the arylalkyne moieties of 11 (H_{o}) shifted upfield in 2a. These upfield shits were observed in many [2]rotaxanes we synthesized. On the other hand, the signal of protons...
of the \( p \)-alkoxyphenyl moieties (\( H_D \)) of 1a shifted downfield in 2a.

![NMR spectra image](image)

**Figure 3-2.** Partial \(^1\)H NMR spectra of [2]rotaxane 2a and related compounds (500 MHz, CDCl\(_3\)).

When the [2]rotaxane 2a was converted to the rotacatenane 3a, the signals of many protons shifted again. The \(^1\)H NMR spectra of rotacatenane 3a, [2]rotaxane 2a and the ring component 1b are shown in Figure 3-3.\(^{17}\) The signals of some protons of 2a and those of many protons of 1b were shifted upfield in 3a. For example, the signals of \( H_{B,C,a} \) of 2a shifted upfield in 3a. Additionally, the signals of the protons of the phenanthroline moiety (\( H_{a-c} \)) and \( p \)-alkoxyphenyl moieties (\( H_e \)) of 1b also shifted upfield in 3a, which is similar to the results observed in the \(^1\)H NMR spectra of 2a (Figure 3-2). In contrast, the signals of protons of the \( p \)-alkoxyphenyl moieties of 2a (\( H_{D,E} \)) and 1b (\( H_d \)) shifted downfield in 3a. We observed the \(^1\)H NMR spectrum of 3b with 2b and 1a, and similar
tendencies were observed for the chemical shifts of those compounds. The $^1$H NMR spectrum of 3b was also different from those of 2b and 1a.$^{18}$

Figure 3-3. Partial $^1$H NMR spectra of rotacatenane 3a and related compounds (500 MHz, CDCl$_3$).
We compared the NMR spectra of the rotacat enane isomers and found that the spectra of the isomers (3a and 3b) were significantly different (Figure 3-4). Some signals of protons of the ring component (1a or 1b) shifted downfield in the presence of the axle component in its cavity. For example, the signal of H_A of 1a appeared at 8.04 ppm in 3a, while the upfield shift of the signal of H_A (ca. 7.94 ppm) was observed in 3b. The signal of H_a of 1b appeared downfield in 3b compared to 3a, which resulted in changing the order of the signals of H_A and H_a between 3a and 3b. The same results was observed in the signals of protons of the phenanthroline moieties of 1a and 1b (H_{B,b}, H_{C,c} and H_{E,e}). The behavior of the signals of H_{D,d} was, however, different from these signals. The signals of H_{D,d} shifted downfield in 3a compared to 3b, which is independent of the connectivity of the components. The signal of protons of the axle component significantly shifted
upfield when the axle component was passing through the smaller ring component (1b). The signal of $H_{ax}$, which was overlapped with other signals, appeared at 6.7 ppm in 3a, and appeared at 6.51 ppm in 3b. We observed similar difference of the chemical shifts in the NMR spectra of [3]rotaxane (type 2. 1).3f

Figure 3-5. Partial $^{13}$C NMR spectra of 3a and 3b (126 MHz, CDCl$_3$).

Compared to the $^1$H NMR spectra, the $^{13}$C NMR spectra was generally less influenced by the difference of the connectivity in the interlocked compounds. Interestingly, we found that the difference of the connectivity influenced the $^{13}$C chemical shifts of 3a and 3b, and the isomeric rotacatenanes could be distinguished by $^{13}$C NMR spectra. Though it was difficult to assign all of the signals, it was possible to assign some signals appeared at 70-82 ppm (Figure 3-5).19 The signal of $C_G$ of the ring component with the alkylene group (1a), which is adjacent to the arylalkyne
moieties, appeared at 79.6 ppm in 3a. This signal appeared at 79.4 ppm in 3b. The signals of carbons of the alkoxyphenyl moieties of the axle component (Cβ,γ) shifted downfield when the axle component was passing through a smaller ring component (1b). The signal of Cβ was observed at 81.7 ppm in 3a, whereas this signal appeared at 81.9 ppm in 3b. The signal of Cγ, which appeared at 73.3 ppm in 3a, also shifted downfield in 3b (73.6 ppm).
3.3 Conclusion

We synthesized a pair of rotacatenane isomers. In our synthesis, two macrocycles were introduced to the interlocked structure by the threading reaction mediated by the macrocyclic metal complex and the metal-template method. The appropriate design of the macrocycles allowed us to introduce the axle moiety to one of the two different rings of a [2]catenane moiety to synthesize sequential rotacatenane isomers. Two rotacatenane isomers were distinguished by $^1$H NMR and $^{13}$C NMR spectroscopy. The study will contribute to the understanding of the chemistry of complex interlocked compounds.
References for Chapter 3


15. 1a-CuI was much less soluble in other halogenated solvents such as dichloromethane and 1,2-dichloroethane.

17. The identification of the signals of 3a and 3b was achieved by NOESY and COSY analysis. In NOESY spectra, the signals of H_E and H_F was correlated with that of the different protons at the etheral position, and the identification of the signals of H_{E,F} was succeeded by COSY analysis. The signals of H_e and H_f were also identified in similar method, and the identification of other signals was carried out based on the results.

18. See Supporting Information.

19. The assignments of these signals were based on the HMBC spectra of 3a and 3b.
Chapter 4

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

4.1 Introduction

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 4-1).1−5 There are many synthetic 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

Figure 4-1. The structure of [2] and [3]rotaxanes
Recently, we reported the synthesis of rotacatenanes, which were composed of a [2]rotaxane component and a ring component (Chapter 2). In our strategy, the coordination ability of a macrocyclic phenanthroline was utilized for both the synthesis of a [2]rotaxane and the installation of another ring component. 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. We have been independently studying a similar synthetic approach and reported the synthesis of [2]rotaxanes using the macrocyclic phenanthroline–Cu complex. As for the installation of another ring component, the metal-template method, which was originally developed by Sauvage, Dietrich-Buchecker, and co-workers and applied to the synthesis of a [2]rotaxane by Gibson and co-workers, was employed. The combination of a copper-mediated catalytic threading approach (also known as active-metal template approach) 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 4-1. A [2]rotaxane is prepared by the oxidative coupling of alkyne using a macrocyclic phenanthroline-CuI complex.\textsuperscript{4e,6m,7} The installation of the second axle is achieved by the metal-template approach,\textsuperscript{12} and metal-free [3]rotaxanes would be isolated after the removal of the metal. In this paper, we report the synthesis of [3]rotaxanes by the above-mentioned strategy.
4.2 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), which we consider as the model system for the synthesis of [3]rotaxane. In order to introduce bulky substituents at final stage of the synthesis of rotaxane, we employed Williamson ether synthesis as the end-capping reaction. The result of the synthesis of [2]rotaxane is summarized in Scheme 4-2.


A tetrahedral Cu(I) complex (4) was prepared in situ from 1a, [Cu(CH$_3$CN)$_4$]PF$_6$ (2), and a phenanthroline derivative (3), and the reaction of 4 with an iodoalkane with a bulky blocking
group (5)\textsuperscript{7m} proceeded in the presence of Cs\textsubscript{2}CO\textsubscript{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.\textsuperscript{13}


With this successful result in hand, we synthesized [3]rotaxanes from [2]rotaxane 7\textit{a} (\textit{n} = 6) or 7\textit{b} (\textit{n} = 20) with 37-membered macrocyclic phenanthroline.\textsuperscript{4e,6,7m} The results are summarized in Scheme 4-3. When [2]rotaxane 7\textit{a} was used as a substrate, [3]rotaxane 9\textit{a} was obtained in 31\% yield. [2]Rotaxane 7\textit{b} with a longer methylene tether also reacted under similar conditions, and the corresponding [3]rotaxane 9\textit{b} was isolated in 20\% yield. The yields of the [3]rotaxanes (9\textit{a} and
9b) 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 and 8b, 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.14

**Synthesis of [2] and [3]Rotaxanes Using Huisgen Cycloaddition.** In order to increase the yields of [3]rotaxanes by suppressing the dissociation of the tetrahedral intermediate, we chose Cu-catalyzed azide-alkyne Huisgen cycloaddition (CuAAC), which usually proceed under milder conditions, as the end-capping reaction.12e,g,k,l,o,15 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 4-4.

The tetrahedral Cu(I) complex 11 was prepared in situ from 1, 2, and a bis(propargyl)phenanthroline derivative 10.16 The end-capping reaction using Huisgen cycloaddition was carried out between 11 and azide 12 in the presence of CuSO4·5H2O 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.17

1a (m = 6)  
1b (m = 6)

1) 2 (1.0 equiv)  
CH₂CN/CH₂Cl₂, rt

2) 10 (1.0 equiv)  
CH₂CN/CH₂Cl₂, rt

12 (2.0 equiv)  
CuSO₄·5H₂O (2.0 equiv)  
ascorbic acid (2.0 equiv)  
DMF (25 mM), rt

2) KCN eq.  
CH₂CN/CH₂Cl₂, rt

13a (63% from 1a)  
13b (76% from 1b)
Scheme 4-5. Synthesis of [3]Rotaxanes by Huisgen Cycloaddition

[3]Rotaxanes were also successfully synthesized by Huisgen cycloaddition. The results are summarized in Scheme 4-5. The tetrahedral Cu(I) complex 14a was prepared in situ from [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 and 15b were similar to that of [2]rotaxane 13a. These results indicated that tetrahedral Cu(I) complexes 14a and 14b 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 and 7d with a smaller ring component \(^{4c,6,7m}\) could be converted to the tetrahedral Cu(I) complexes 14c and 14d,\(^{18}\) and [3]rotaxanes 15c and 15d were isolated in about 70% yields from 7c and 7d, respectively. It is noteworthy that rotacatenanes were not synthesized from 7c and 7d,\(^{6}\) whereas we succeeded in the synthesis of [3]rotaxanes from 7c and 7d.


In order to understand the reason for the observed results, we studied the synthesis of [3]rotaxanes from 7, diyne 16,\(^{6}\) and 12 (Scheme 4-6). 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 tetrahedral Cu(I) complex was assumed to be the reason for the unsuccessful result. 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%). 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 1H NMR spectra of 14e and 14f. The 1H 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. 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, 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 and 9b compared to those of 15a and 15b 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.
**1H 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 4-2.

![1H NMR Spectra of [3]rotaxane 15b and related compounds.](image)

As observed in many interlocked compounds we prepared, most signals of 7b, 13a, and 18 shifted upfield in [3]rotaxane 15b. For example, the signals of the $p$-alkoxyphenyl moiety (H_{d,e}), the phenanthroline moiety of 7b (H_{a-c}), and the phenanthroline moiety of 13a and 18 (H_{k-m}) shifted upfield in 15b. In contrast, the signal of one proton of the resorcinol moiety of a macrocyclic
phenanthroline (H\textsubscript{f}) shifted downfield. The downfield shift of H\textsubscript{f} was also observed in some interlocked compounds we synthesized.\textsuperscript{4e,6,7a,m,9,12f} 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\textsubscript{p}) of 18 also significantly shifted downfield in 15b.\textsuperscript{21} The downfield shift of H\textsubscript{p}, which was also observed in \textsuperscript{1}H NMR spectra of [2]rotaxane 13a, would be caused by the formation of the hydrogen bond between H\textsubscript{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.\textsuperscript{7c,f,i,q,22}
Figure 4-3. (a) $^1$H NMR spectra of 15b, 15d, 13a, 13b and 18 (500 MHz, CDCl$_3$). (b) $^1$H NMR spectra of 15e, 15f and unthreaded axle component 19 (500 MHz, CDCl$_3$).
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 (\(13a, 13b, 15b\) and \(15d\)), and the unthreaded axle component \(18\), which are shown in Figure 4-3a. 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 \( H_o \),\(^{23}\) 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 \(15e\) and \(15f\) (Figure 4-3b). We assume that the increased flexibility of the axle components resulted in the reduced interaction between \( H_p' \) and the phenanthroline moiety.
4.3 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 and the triazole 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.
References for Chapter 4


13. [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).

14. Decomposition of 5 and tetrahedral Cu(I) complex was observed during the monitoring of the end-capping reaction. Demetalation of 8 (or mono-alkylated 8) might proceed due to the presence of Cs₂CO₃ and hot DMF before the formation of the [3]rotaxane 9-Cu(I) complex.


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

18. In ¹H NMR spectra of the crude product, we confirmed that 14c and 14d were the major products.

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

20. 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 Cu(I) complex composed of two 16, was observed during the monitoring of the reaction (TLC and 1H NMR analysis). The observed results might be attributed to another factor such as the relative activation barrier for the formation of 14e and 14f. 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 and 14f are under investigation.

21. In the HMBC spectra of 13a, the signal of H q, which was observed at 5.05 ppm in 1H NMR spectrum, correlated with a quaternary carbon atom of a triazole moiety of which the signal was observed at 143.53 ppm in 13C NMR spectrum. Another singlet signal, which appeared at 7.62 ppm in 1H NMR spectrum, 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 1H NMR spectra of 18 and another phenanthroline derivative.


23. The signals of H p and H o were separated in a 1H NMR analysis which was performed in DMSO-d6/CDCl3 (see the Supporting Information).
SI-Chapter 2

General Procedure

Commercially available reagents were used without further purification unless otherwise noted. Macrocyclic phenanthroline-CuI complex (1a),1 alkynes (2a-c),1,2 [2-(12-bromododecyloxy)phenylethynyl]trimethylsilane,3 4,4’-(1,10-phenanthroline-2,9-diyl)dipheno| HCl salt,1,4 macrocyclic phenanthrolines (4a and 4b)5 were prepared as reported. NMR chemical shifts were reported in delta units (δ) relative to chloroform-d (7.24 ppm for 1H NMR and 77.0 ppm for 13C NMR). Multiplicity is indicated by s (singlet), d (doublet), t (triplet) quin (quintet) or m (multiplet). Coupling constants, J, are reported in Hz. A recycling preparative HPLC, equipped with high-resolution GPC column(s) (exclusion limit: 1000 or 5000 MW), was used for the GPC separation. Column chromatography was performed using silica gel 60N (spherical, neutral 63-210 μm). Preparative thin layer chromatography (PTLC) was performed using a Merck silica gel 60 plate.


Macrocyclic phenanthroline-CuI complex 1b

The reported procedure1 was generally followed to synthesize 1b. To a solution of macrocyclic phenanthroline 4b (0.91 g, 1.3 mmol) in CH2Cl2 (60 mL) was added the solution of CuI (0.25 g, 1.3 mmol) in CH3CN (24 mL). After stirring for 1 h at room temperature, the solvent was removed in vacuo. The resulting residue was recrystallized from hexane and CH2Cl2 to afford 1b (1.0 g, 1.2 mmol) in 91% yield as an orange solid.

mp 100.4-101.3 °C; 1H NMR (300 MHz, CDCl3) δ 8.42 (d, J = 8.4 Hz, 2H), 8.14 (d, J = 8.7 Hz, 4H), 8.10 (d, J = 8.4 Hz, 2H), 7.88 (s, 2H), 7.16-7.07 (m, 5H), 6.51-6.43 (m, 3H), 4.05 (t, J = 6.9 Hz, 4H), 3.95 (t, J = 6.5 Hz, 4H), 1.87-1.72 (m, 8H), 1.55-1.40 (m, 16H); 13C NMR (126 MHz, CDCl3) δ 160.8, 160.3, 157.1, 143.2, 137.8, 130.9, 129.6, 129.3, 126.8, 125.7, 123.6, 114.4, 106.9, 100.5, 68.0, 67.8, 29.2, 29.13, 29.07, 29.0, 25.7, 25.6; IR (ATR) 3038, 2927, 2854, 1602, 1584, 1487, 1470, 1249, 1173, 1146, 1022, 831, 796, 747, 686, 516 cm−1; Anal. Calcd for
C_{46}H_{50}N_{2}CuIO_{4} \cdot 1/2H_{2}O: C, 61.78; H, 5.75; N, 3.13. Found: C, 61.59; H, 5.68; N, 3.09.

[2] Rotaxane 3a (procedure A)

General procedure was reported in the reference. A mixture of 2a (34 mg, 0.050 mmol), macrocyclic phenanthroline-CuI complex 1a (17 mg, 0.020 mmol), K_{2}CO_{3} (10 mg, 0.075 mmol) and I_{2} (6.3 mg, 0.025 mmol) in dry xylene (1.0 mL) under Ar atmosphere was stirred at 130 °C for 48 h. The solution was cooled to room temperature and CH_{2}Cl_{2} (1.5 mL), CH_{3}CN (3.5 mL) and aqueous ammonia (30% solution, 1.7 mL) was added to the solution. After stirring at room temperature for overnight, the solution was extracted with CH_{2}Cl_{2}. The combined organic layer was washed with water, dried over Na_{2}SO_{4}, and concentrated. The residue was purified by silica gel column chromatography using hexane and CH_{2}Cl_{2} (3/1 (v/v)) and GPC using CHCl_{3} to afford 3a (29 mg, 0.014 mmol) in 72% yield as a colorless amorphous solid. The analytical data were identical with those reported in the reference.

[2] Rotaxane 3b

Procedure A was generally followed to synthesize 3b from 2b (56 mg, 0.050 mmol) and 1a (17 mg, 0.020 mmol). The product was purified by silica gel column chromatography using hexane and CH_{2}Cl_{2} (1/1 (v/v)) and GPC using CHCl_{3} to afford 3b (44 mg, 0.015 mmol) in 76% yield as a yellow amorphous solid.
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.42 (d, $J = 8.5$ Hz, 4H), 8.20 (d, $J = 8.5$ Hz, 2H), 8.03 (d, $J = 8.5$ Hz, 2H), 7.70 (s, 2H), 7.52-7.43 (m, 24H), 7.40 (d, $J = 8.5$ Hz, 4H), 7.33 (d, $J = 8.5$ Hz, 12H), 7.26-7.19 (m, 12H), 7.11 (t, $J = 8.0$ Hz, 1H), 7.02 (d, $J = 8.5$ Hz, 4H), 6.75 (d, $J = 9.5$ Hz, 4H), 6.56 (t, $J = 2.0$ Hz, 1H), 6.46 (dd, $J = 8.3$ Hz, 2.3 Hz, 2H), 3.99-3.91 (m, 8H), 2.63-2.55 (m, 4H), 2.54-2.45 (m, 6H), 1.96-1.70 (m, 38H), 1.70-1.62 (m, 4H), 1.58-1.05 (m, 106H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 160.42, 160.37, 159.8, 156.2, 147.0, 146.4, 146.0, 138.3, 138.2, 136.6, 134.0, 132.0, 129.7, 129.6, 128.9, 127.4, 127.1, 126.8, 126.2, 125.5, 119.1, 114.68, 114.66, 113.6, 107.0, 101.1, 81.5, 73.2, 68.1, 68.0, 67.7, 56.0, 44.2, 40.5, 34.4, 30.5, 29.74, 29.71, 29.69, 29.67, 29.65, 29.60, 29.56, 29.4, 29.2, 29.1, 26.9, 26.2, 26.0, 25.93, 25.88, 25.8; IR(KBr) 3433, 3024, 2924, 2854, 2137, 1905, 1597, 1496, 1288, 1250, 1173, 1003, 810, 733, 532 cm$^{-1}$; HR-MS (MALDI-TOF) Calcd for C$_{208}$H$_{245}$N$_2$O$_6$ ([M + H]$^+$): 2866.8922. Found: 2866.9247.

[2]Rotaxane 3c

Procedure A was generally followed to synthesize 3c from 2c (46 mg, 0.050 mmol) and 1b (18 mg, 0.020 mmol). The product was purified by silica gel column chromatography using hexane and CH$_2$Cl$_2$ (1/1 (v/v)) and GPC using CHCl$_3$ to afford 3c (14 mg, 5.5 $\mu$mol) in 27% yield as a yellow amorphous solid. The analytical data were identical with those reported in the reference.$^{2a}$

[2]Rotaxane 3d

Procedure A was generally followed to synthesize 3d from 2b (56 mg, 0.050 mmol) and 1b (18...
The product was purified by silica gel column chromatography using hexane and CH₂Cl₂ (1/1 (v/v)) and GPC using CHCl₃ to afford 3d (25 mg, 8.6 μmol) in 43% yield as a yellow amorphous solid.

\( ^1H \text{ NMR (500 MHz, CDCl}_3 \) \( \delta 8.42 \) (d, \( J = 8.5 \) Hz, 4H), 8.20 (d, \( J = 8.0 \) Hz, 2H), 8.03 (d, \( J = 8.5 \) Hz, 2H), 7.69 (s, 2H), 7.49 (d, \( J = 9.0 \) Hz, 12H), 7.47 (d, \( J = 8.5 \) Hz, 12H), 7.39 (d, \( J = 8.5 \) Hz, 4H), 7.33 (d, \( J = 8.5 \) Hz, 12H), 7.23 (d, \( J = 9.0 \) Hz, 12H), 7.10 (t, \( J = 8.3 \) Hz, 1H), 7.02 (d, \( J = 8.5 \) Hz, 4H), 6.75 (d, \( J = 8.6 \) Hz, 4H), 6.47 (t, \( J = 2.0 \) Hz, 1H), 6.45 (dd, \( J = 8.8 \) Hz, 2.3 Hz, 2H), 3.96 (t, \( J = 6.5 \) Hz, 4H), 3.90 (t, \( J = 6.5 \) Hz, 4H), 3.84 (t, \( J = 6.8 \) Hz, 4H), 2.63-2.55 (m, 4H), 2.54-2.45 (m, 6H), 1.95-1.63 (m, 42H), 1.50-1.06 (m, 114H); \( ^{13}C \text{ NMR (126 MHz, CDCl}_3 \) \( \delta 160.43, 160.36, 159.7, 156.1, 146.9, 146.3, 145.9, 138.3, 138.1, 136.6, 133.9, 131.8, 129.6, 129.5, 128.9, 127.3, 127.1, 126.7, 126.1, 125.5, 119.0, 114.6, 114.5, 113.5, 106.8, 100.8, 81.4, 73.1, 68.0, 67.9, 67.7, 55.9, 44.1, 40.5, 34.4, 30.5, 29.71, 29.68, 29.66, 29.64, 29.58, 29.54, 29.52, 29.33, 29.29, 29.1, 26.8, 26.1, 25.9, 25.82, 25.79, 25.7; IR (KBr) 3024, 2924, 2846, 1597, 1496, 1466, 1288, 1250, 1173, 1003, 532 cm\(^{-1}\); HR-MS (MALDI-TOF) Calcd for C\(_{212}\)H\(_{253}\)N\(_2\)O\(_6\) ([M + H\(^+\)]: 2922.9548. Found: 2922.9626.


Diyne 6

A mixture of 4,4’-(1,10-phenanthroline-2,9-diyl)diphenol HCl salt (0.16 g, 0.39 mmol), [2-(12-bromo-dodecyloxy)phenylethynyl]trimethylsilane (0.51 g, 1.2 mmol) and K\(_2\)CO\(_3\) (0.82 g, 5.9 mmol) was dissolved in DMSO (4.6 mL), and the solution was heated to 70 °C. After 4 h, the solvent was removed in vacuo. Water was added to the yellow residue and the aqueous layer was extracted with CH₂Cl₂. The combined organic phase was washed with water, dried over Na\(_2\)SO\(_4\), and concentrated. The residue was purified by silica gel chromatography using hexane and CH₂Cl₂ (1/2 (v/v)) to afford 6 (0.29 g, 0.31 mmol) in 80% yield as a colorless solid.

mp 106.0-108.0 °C; \(^1H \text{ NMR (300 MHz, CDCl}_3 \) \( \delta 8.42 \) (d, \( J = 9.0 \) Hz, 4H), 8.23 (d, \( J = 8.4 \) Hz, 2H), 8.06 (d, \( J = 8.4 \) Hz, 2H), 7.72 (s, 2H), 7.42 (dd, \( J = 7.8 \) Hz, 1.5 Hz, 2H), 7.29-7.72 (m, 2H), 7.08 (d, \( J = 9.0 \) Hz, 4H), 6.90-6.82 (m, 4H), 4.10-3.90 (m, 8H), 3.24 (s, 2H), 1.90-1.75 (m, 8H), 1.55-1.20 (m, 32H); \( ^{13}C \text{ NMR (126 MHz, CDCl}_3 \) \( \delta 160.4, 160.1, 156.2, 145.9, 136.6, 133.9, 131.8, 130.0, 128.8, 127.3, 125.4, 120.1, 119.1, 114.6, 111.9, 111.6, 80.9, 80.1, 68.6, 68.0, 29.5, 29.4, 29.3, 29.21, 29.18, 29.0, 25.9, 25.8; IR (KBr) 3433, 3294, 3062, 3039, 2924, 2854, 2561, 2106, 1597,
Tetrahedral Cu(I) complex 7a (procedure B)

To a solution of [Cu(CH3CN)4]PF6 (15 mg, 0.039 mmol) in dry CH3CN (3.1 mL) was added a solution of 4a (25 mg, 0.039 mmol) in dry CH2Cl2 (3.1 mL) at room temperature. The color of the mixture immediately turned into yellow. After stirring for 30 min at room temperature, a solution of 6 (36 mg, 0.039 mmol) in dry CH2Cl2 (3.1 mL) was added to the reaction mixture, producing a color change to dark purple. The resulting mixture was stirred for 1 h. The solvent was removed in vacuo. The residue was purified by silica gel column chromatography using CH2Cl2 to afford the product 7a (58 mg, 0.033 mmol) in 84% yield as a purple amorphous solid.

1H NMR (500 MHz, CDCl3) δ 8.40 (d, J = 8.0 Hz, 2H), 8.29 (d, J = 8.0 Hz, 2H), 7.93 (s, 2H), 7.84-7.79 (m, 4H), 7.77 (d, J = 8.5 Hz, 2H), 7.44-7.35 (m, 10H), 7.29-7.22 (m, 3H), 6.89-6.83 (m, 4H), 6.81 (t, J = 2.3 Hz, 1H), 6.63 (dd, J = 8.5 Hz, 2.5 Hz, 2H), 6.00 (d, J = 9.5 Hz, 4H), 5.98 (d, J = 9.0 Hz, 4H), 4.13 (t, J = 6.0 Hz, 4H), 4.02 (t, J = 6.8 Hz, 4H), 3.52 (t, J = 6.3 Hz, 4H), 3.47 (t, J = 6.3 Hz, 4H), 3.23 (s, 2H), 1.90 (quin, J = 6.6 Hz, 4H), 1.82 (quin, J = 7.0 Hz, 4H), 1.66-1.52 (m, 12H), 1.52-1.41 (m, 8H), 1.40-1.26 (m, 28H); 13C NMR (126 MHz, CDCl3) δ 160.6, 160.2, 159.8, 159.7, 156.4, 136.9, 136.8, 134.0, 130.3, 130.1, 129.2, 127.8, 125.9, 120.2, 112.9, 112.8, 112.0, 111.6, 106.8, 101.8, 80.9, 80.2, 68.7, 67.9, 67.8, 67.6, 29.57, 29.55, 29.5, 29.33, 29.28, 29.02, 29.00, 28.9, 28.5, 26.0, 25.9, 25.7, 25.3; IR(KBr) 3310, 2932, 2861, 1734, 1602, 1587, 1250, 1175, 1151, 1017, 838 cm−1; HR-MS (ESI): Calcd. For C106H114N4O8Cu ([M - PF6]+): 1633.7927. Found: 1633.7927.

Tetrahedral Cu(I) complex 7b

Procedure B was generally followed to synthesize 7b from [Cu(CH3CN)4]PF6 (19 mg, 0.050
mmol), 4b (35 mg, 0.050 mmol) and 6 (47 mg, 0.050 mmol). The product was purified by silica gel column chromatography using CH$_2$Cl$_2$ to afford 7b (84 mg, 0.046 mmol) in 91% yield as a purple amorphous solid.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.40 (d, $J = 8.0$ Hz, 2H), 8.37 (d, $J = 8.0$ Hz, 2H), 7.92 (s, 2H), 7.88 (s, 2H), 7.85-7.79 (m, 4H), 7.42 (dd, $J = 8.0$ Hz, 2.0 Hz, 2H), 7.40-7.34 (m, 8H), 7.26 (td, $J = 8.0$ Hz, 1.3 Hz, 2H), 7.18 (t, $J = 8.3$ Hz, 1H), 6.89-6.82 (m, 4H), 6.63 (t, $J = 2.5$ Hz, 1H), 6.54 (dd, $J = 8.5$ Hz, 2.5 Hz, 2H), 6.04-5.96 (m, 8H), 4.06 (t, $J = 6.3$ Hz, 4H), 4.01 (t, $J = 6.8$ Hz, 4H), 3.54 (t, $J = 6.8$ Hz, 4H), 3.48 (t, $J = 6.8$ Hz, 4H), 3.23 (s, 2H), 1.91-1.78 (m, 8H), 1.67-1.56 (m, 12H), 1.52-1.25 (m, 44H); 13C NMR (126 MHz, CDCl$_3$) $\delta$ 160.5, 160.3, 159.81, 159.76, 156.47, 156.45, 143.48, 143.46, 136.9, 136.8, 134.0, 131.0, 130.1, 129.9, 129.19, 129.17, 127.8, 127.7, 125.94, 125.93, 124.4, 124.3, 120.2, 113.0, 112.9, 112.1, 111.7, 107.0, 101.5, 80.9, 80.2, 68.8, 68.0, 67.9, 67.8, 29.60, 29.55, 29.4, 29.3, 29.2, 29.14, 29.12, 29.08, 29.0, 28.9, 26.1, 26.0, 25.9, 25.8; IR(KBr) 3433, 3278, 3070, 2931, 2854, 2106, 1604, 1489, 1389, 1358, 1281, 1262, 1211, 1180, 1111, 1026, 849, 756, 648, 555 cm$^{-1}$; HR-MS (ESI) Calcd for C$_{110}$H$_{122}$N$_4$O$_8$Cu ([M - PF$_6$]$^+$): 1689.85532. Found: 1689.85468.

[2] Catenane 8a (procedure C)

A mixture of tetrahedral Cu(I) complex 7a (14 mg, 7.9 $\mu$mol), CuCl (78 mg, 0.79 mmol) and CuCl$_2$ (13 mg, 0.094 mmol) in dry DMF (16 mL) was stirred at room temperature. After 72 h, the solvent was removed in vacuo. Water was added to the residue and the aqueous layer was extracted with CH$_2$Cl$_2$. The combined organic phase was washed with water, dried over MgSO$_4$, and concentrated. The residue was purified by short silica gel chromatography using CH$_2$Cl$_2$ and AcOEt (50/1 (v/v)), and CH$_3$CN (2.0 mL), CH$_2$Cl$_2$ (2.0 mL), H$_2$O (2.0 mL) and KCN (23 mg) were added to the residue. The solution was stirred at room temperature for overnight. Water was added to the resulting solution and the aqueous layer was extracted with CH$_2$Cl$_2$. The combined organic layer was washed with water, dried over Na$_2$SO$_4$, and concentrated. The residue was purified by silica gel column chromatography using CH$_2$Cl$_2$ and AcOEt (50/1 (v/v)) to afford the product 8a (5.6 mg, 3.6 $\mu$mol) in 45% yield as a pale yellow amorphous solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.46-8.39 (m, 8H), 8.22-8.15 (m, 4H), 8.06-7.99 (m, 4H), 7.69 (s, 2H), 7.68 (s, 2H), 7.44 (dd, $J = 7.6$ Hz, 2.0 Hz, 2H), 7.21 (ddd, $J = 8.4$ Hz, 7.5 Hz, 1.5 Hz, 2H), 7.14 (t, $J = 8.2$ Hz, 1H), 7.05 (d, $J = 8.8$ Hz, 4H), 6.98 (d, $J = 8.8$ Hz, 4H), 6.82 (td, $J = 7.6$ Hz, 0.8 Hz, 2H), 6.77 (d, $J = 8.0$ Hz, 2H), 6.70 (t, $J = 2.2$ Hz, 1H), 6.49 (dd, $J = 8.2$ Hz, 2.2 Hz, 2H), 3.99
(t, \( J = 6.2 \text{ Hz}, 4\H), 3.96-3.84 \text{ (m, 12H), 1.84-1.64 \text{ (m, 16H), 1.57-1.11 \text{ (m, 40H); \( ^{13}\text{C NMR (126 MHz, CDCl}_3\) } \delta 160.9, 160.51, 160.50, 160.3, 156.31, 156.25, 146.0, 136.7, 134.5, 132.0, 131.8, 130.4, 129.8, 129.0, 127.41, 127.40, 125.5, 120.3, 119.2, 114.8, 114.7, 111.9, 111.6, 107.0, 101.2, 78.9, 78.1, 68.8, 68.1, 67.9, 67.8, 29.64, 29.61, 29.5, 29.32, 29.30, 29.2, 28.9, 26.03, 25.98, 25.80, 25.77; IR(KBr) 2925, 2852, 1587, 1488, 1281, 1250, 1174, 1020, 837, 749, 416 \text{ cm}^{-1}; \) HR-MS (FAB); Calcd. For \( \text{C}_{106}\text{H}_{113}\text{N}_4\text{O}_{10} \text{ ([M + H]^+): 1569.8558. Found: 1569.8560.}

\[\text{[2]Catenane 8b}\]

Procedure C was generally followed to synthesize 8b from tetrahedral Cu(I) complex 7b (19 mg, 0.010 mmol). The product was purified by silica gel column chromatography using CH\(_2\)Cl\(_2\) and AcOEt (50/1 \(v/v\)) to afford 8b (8.3 mg, 5.1 \( \mu \text{mol}\) ) in 51% yield as a pale yellow solid.

mp 87.0-88.1 °C; \(^1\text{H NMR (500 MHz, CDCl}_3\) } \delta 8.47-8.39 \text{ (m, 8H), 8.23-8.15 \text{ (m, 4H), 8.07-7.98 \text{ (m, 4H), 7.68 \text{ (s, 2H), 7.67 \text{ (s, 2H), 7.45 \text{ (dd, } J = 8.0 \text{ Hz, 1.5 Hz, 2H), 7.26-7.18 \text{ (m, 2H), 7.14 \text{ (t, } J = 8.0 \text{ Hz, 1H), 7.06-6.98 \text{ (m, 8H), 6.84 \text{ (t, } J = 7.8 \text{ Hz, 2H), 6.79 \text{ (d, } J = 8.0 \text{ Hz, 2H), 6.61 \text{ (t, } J = 2.3 \text{ Hz, 1H), 6.48 \text{ (dd, } J = 8.0 \text{ Hz, 2.0 Hz, 2H), 3.98-3.90 \text{ (m, 8H), 3.87 \text{ (t, } J = 7.0 \text{ Hz, 4H), 3.83 \text{ (t, } J = 6.5 \text{ Hz, 4H), 1.80-1.61 \text{ (m, 16H), 1.45-1.09 \text{ (m, 48H); \( ^{13}\text{C NMR (126 MHz, CDCl}_3\) } \delta 160.9, 160.52, 160.51, 160.47, 156.24, 156.19, 146.1, 136.61, 136.58, 134.5, 131.83, 131.81, 130.4, 129.8, 128.9, 127.41, 127.39, 125.5, 120.3, 119.1, 119.0, 114.8, 114.7, 112.0, 111.7, 106.9, 101.0, 78.8, 78.1, 68.8, 68.0, 67.9, 67.8, 29.64, 29.61, 29.59, 29.50, 29.48, 29.39, 29.37, 29.36, 29.32, 29.29, 29.27, 29.0, 25.94, 25.89, 25.8, 25.7; IR(KBr) 3433, 3062, 3039, 2924, 2854, 2214, 2144, 1936, 1898, 1720.19, 1597, 1489, 1396, 1281, 1250, 1173, 1119, 1026, 841, 795, 748, 517, 463 \text{ cm}^{-1}; \) HR-MS (ESI) Calcd for \( \text{C}_{110}\text{H}_{121}\text{N}_4\text{O}_8 \text{ ([M + H]^+): 1625.91789. Found: 1625.91789.}

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Synthesis of Rotacatenanes.
Tetrahedral Cu(I) complex 9c (procedure D)

To a solution of [Cu(CH3CN)4]PF6 (2.4 mg, 6.4 μmol) in dry CH3CN (1.0 mL) was added a solution of 3c (16 mg, 6.4 μmol) in dry CH2Cl2 (2.0 mL) at room temperature. The color of the mixture immediately turned into yellow. After stirring for 3 h at room temperature, a solution of 6 (6.0 mg, 6.4 μmol) in dry CH2Cl2 (2.0 mL) was added to the reaction mixture, producing a color change to dark red. The resulting mixture was stirred for 1 h. The solvent was removed in vacuo. The residue was purified by silica gel column chromatography using CH2Cl2 and AcOEt (50/1 (v/v)) to afford 9c (19 mg, 5.2 μmol) in 83% yield as a dark red amorphous solid.

1H NMR (500 MHz, CDCl3) δ 8.39 (d, J = 8.5 Hz, 2H), 8.13 (d, J = 8.0 Hz, 2H), 7.89 (s, 2H), 7.79 (d, J = 9.0 Hz, 2H), 7.68-7.61 (m, 4H), 7.52-7.45 (m, 24H), 7.42 (dd, J = 7.8 Hz, 1.8 Hz, 2H), 7.33 (d, J = 9.0 Hz, 12H), 7.31-7.21 (m, 22H), 7.15-7.09 (m, 5H), 6.88-6.82 (m, 4H), 6.67 (t, J = 2.3 Hz, 1H), 6.59 (d, J = 8.5 Hz, 4H), 6.49 (dd, J = 8.0 Hz, 2.5 Hz, 2H), 6.03 (d, J = 8.5 Hz, 4H), 6.00 (d, J = 8.5 Hz, 4H), 4.01 (t, J = 6.8 Hz, 4H), 3.97 (t, J = 6.5 Hz, 4H), 3.72 (t, J = 6.8 Hz, 4H), 3.54 (t, J = 6.3 Hz, 4H), 3.49 (t, J = 6.8 Hz, 4H), 3.22 (s, 2H), 2.64-2.56 (m, 4H), 2.55-2.45 (m, 6H), 1.95-1.68 (m, 38H), 1.66-1.56 (m, 12H), 1.56-1.11 (m, 90H); 13C NMR (126 MHz, CDCl3) δ 160.5, 160.2, 159.8, 159.7, 159.6, 156.5, 156.4, 147.1, 146.2, 143.5, 143.4, 138.4, 138.1, 137.0, 136.8, 134.0, 133.8, 131.2, 131.0, 130.1, 129.7, 129.5, 129.0, 128.9, 127.8, 127.6, 127.2, 126.8, 126.2, 126.0, 125.8, 124.5, 124.3, 120.2, 114.6, 113.2, 113.04, 113.00, 112.0, 111.6, 107.1, 101.3, 81.8, 80.9, 80.2, 73.6, 68.7, 68.01, 67.95, 67.9, 67.7, 56.0, 44.2, 40.4, 34.4, 30.2, 29.7, 29.61, 29.55, 29.4, 29.3, 29.2, 29.11, 29.05, 26.9, 26.14, 26.07, 25.9, 25.7; IR(KBr) 3433, 3309, 3024, 2924, 2854, 2137, 2106, 1905, 1604, 1496, 1250, 1173, 1011, 841, 756, 555 cm⁻¹; HR-MS (MALDI-TOF) Calcd for C248H268N4O10Cu ([M - PF6]⁺): 3525.9954. Found: 3525.9887.
Tetrahedral Cu(I) complex 9d

Procedure D was generally followed to synthesize 9d from [Cu(CH3CN)₄]PF₆ (2.6 mg, 6.9 μmol), 3d (20 mg, 6.9 μmol) and 6 (6.3 mg, 6.9 μmol). The product was purified by silica gel column chromatography using CH₂Cl₂ and AcOEt (50/1 (v/v)) to afford 9d (25 mg, 6.1 μmol) in 88% yield as a dark red amorphous solid.

1H NMR (500 MHz, CDCl₃) δ 8.41 (d, J = 8.5 Hz, 2H), 8.20 (d, J = 8.0 Hz, 2H), 7.90 (s, 2H), 7.82 (d, J = 8.5 Hz, 2H), 7.71 (s, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.53-7.45 (m, 24H), 7.42 (dd, J = 8.0 Hz, 1.5 Hz, 2H), 7.38-7.29 (m, 20H), 7.29-7.20 (m, 14H), 7.19-7.13 (m, 5H), 6.88-6.83 (m, 4H), 6.67 (t, J = 2.3 Hz, 1H), 6.65 (d, J = 8.5 Hz, 4H), 6.51 (dd, J = 8.0 Hz, 2.0 Hz, 2H), 6.05 (d, J = 8.5 Hz, 4H), 6.02 (d, J = 8.5 Hz, 4H), 4.05-3.96 (m, 8H), 3.79 (t, J = 6.3 Hz, 4H), 3.56 (t, J = 6.5 Hz, 4H), 3.51 (t, J = 6.5 Hz, 4H), 3.23 (s, 2H), 2.64-2.56 (m, 4H), 2.55-2.46 (m, 6H), 1.94-1.78 (m, 32H), 1.77-1.71 (m, 6H), 1.70-1.59 (m, 12H), 1.58-1.08 (m, 146H); 13C NMR (126 MHz, CDCl₃) δ 160.5, 160.2, 159.9, 159.7, 159.6, 156.5, 156.4, 147.0, 146.4, 143.5, 143.4, 138.4, 138.2, 137.0, 136.9, 134.0, 133.8, 131.2, 131.0, 130.1, 129.7, 129.6, 129.0, 128.9, 127.8, 127.6, 127.1, 126.8, 126.2, 126.0, 125.9, 124.5, 124.4, 120.2, 114.6, 113.2, 113.04, 113.00, 112.0, 111.6, 107.1, 101.4, 81.8, 80.9, 80.2, 73.5, 68.7, 68.1, 68.0, 67.9, 67.7, 56.0, 44.2, 40.5, 34.4, 30.5, 29.7, 29.62, 29.60, 29.55, 29.54, 29.50, 29.41, 29.39, 29.3, 29.2, 29.09, 29.05, 29.0, 26.9, 26.2, 26.14, 26.07, 26.0, 25.9, 25.7; IR(KBr) 3433, 3024, 2924, 2854, 2137, 2106, 1905, 1604, 1496, 1281, 1250, 1173, 1003, 841, 748, 555 cm⁻¹; HR-MS (MALDI-TOF) Calcd for C₂₇₆H₃₂₄NaO₁₀Cu ([M - PF₆]⁺): 3917.4258. Found: 3917.4660.
Rotacatenane 10c (procedure E).

A mixture of tetrahedral Cu(I) complex 9c (20 mg, 5.3 μmol), CuCl (52 mg, 0.53 mmol) and CuCl2 (8.6 mg, 0.064 mmol) in dry DMF (10 mL) was stirred at room temperature. After 72 h, the solvent was removed in vacuo. Water was added to the residue and the aqueous layer was extracted with CH2Cl2. The combined organic phase was washed with water, dried over MgSO4, and concentrated. The residue was purified by short silica gel chromatography using CH2Cl2 and AcOEt (50/1 (v/v)) and CH3CN (2.0 mL), CH2Cl2 (2.0 mL), H2O (2.0 mL) and KCN (23 mg) were added to the residue. The solution was stirred at room temperature for overnight. Water was added to the solution and the aqueous layer was extracted with CH2Cl2. The combined organic layer was washed with water, dried over Na2SO4, and concentrated. The residue was purified by silica gel column chromatography using CH2Cl2 and AcOEt (50/1 (v/v)) and preparative thin layer chromatography using CH2Cl2 and AcOEt (50/1 (v/v)) to afford the rotacatenane 10c (7.4 mg, 2.1 μmol) in 40% yield as a yellow amorphous solid.

1H NMR (500 MHz, CDCl3) δ 8.37 (d, J = 8.5 Hz, 8H), 8.15 (d, J = 8.0 Hz, 2H), 8.10 (d, J = 8.0 Hz, 2H), 7.98 (d, J = 8.5 Hz, 2H), 7.94 (d, J = 8.5 Hz, 2H), 7.64 (s, 2H), 7.61 (s, 2H), 7.50-7.42 (m, 24H), 7.40 (dd, J = 7.5 Hz, 1.5 Hz, 2H), 7.32-7.26 (m, 16H), 7.22 (d, J = 8.0 Hz, 12H), 7.15 (t, J = 8.1 Hz, 2H), 7.09 (t, J = 8.5 Hz, 1H), 7.04-6.99 (m, 8H), 6.76 (t, J = 7.5 Hz, 2H), 6.74-6.70 (m, 3H), 6.61 (d, J = 9.5 Hz, 4H), 6.45 (dd, J = 8.0 Hz, 2.0 Hz, 2H), 3.98 (t, J = 7.0 Hz, 4H), 3.91 (t, J = 6.5 Hz, 8H), 3.86 (t, J = 7.0 Hz, 4H), 3.66 (t, J = 6.8 Hz, 4H), 2.55-2.45 (m, 10H), 1.93-1.79 (m, 24H), 1.79-1.63 (m, 22H), 1.61-1.00 (m, 94H); 13C NMR (126MHz, CDCl3) δ 160.8, 160.6, 160.5, 160.4, 159.6, 156.6, 156.2, 147.0, 146.3, 146.0, 138.4, 138.1, 136.6, 136.5, 134.5, 134.0, 131.9, 131.7, 130.3, 129.5, 129.0, 128.9, 127.5, 127.3, 127.2, 126.8, 126.2, 125.5, 125.4, 120.2, 119.4, 119.0, 114.70, 114.67, 114.5, 113.5, 111.8, 111.5, 107.1, 101.0, 81.7, 79.0, 78.2, 73.7, 68.7, 68.1, 68.01, 67.97, 67.9, 55.9, 44.2, 40.4, 34.4, 30.2, 29.9, 29.83, 29.79, 29.7, 29.63, 29.55, 29.5, 29.40, 29.37, 29.2, 28.9, 26.9, 26.14, 26.10, 26.08, 25.9, 25.8, 25.7; IR(KBr) 3433, 3032, 2924, 2854, 2206, 2144, 1905, 1728, 1597, 1496, 1281, 1250, 1173, 1011, 833, 818, 748, 532 cm⁻¹; HR-MS (MALDI-TOF) Calcd for C248H267N4O10 ([M + H]⁺): 3461.0502. Found: 3461.0447.
Procedure E was generally followed to synthesize 10d from 9d (23 mg, 5.6 μmol). The product was purified by silica gel column chromatography using CH₂Cl₂ and AcOEt (50/1 (v/v)) and preparative thin layer chromatography using CH₂Cl₂ and AcOEt (50/1(v/v)) to afford 10d (6.3 mg, 1.6 μmol) in 29% yield as a yellow amorphous solid.

¹H NMR (500 MHz, CDCl₃) δ 8.43-8.36 (m, 8H), 8.20-8.14 (m, 4H), 8.03-7.98 (m, 4H), 7.672 (s, 2H), 7.666 (s, 2H), 7.49 (d, J = 8.0 Hz, 12H), 7.47 (d, J = 8.5 Hz, 12H), 7.42 (dd, J = 7.5 Hz, 2.0 Hz, 2H), 7.36-7.30 (m, 16H), 7.26-7.20 (m, 12H), 7.17 (t, J = 7.6 Hz, 2H), 7.10 (t, J = 8.0 Hz, 1H), 7.08-7.01 (m, 8H), 6.78 (t, J = 7.5 Hz, 2H), 6.76-6.71 (m, 3H), 6.65 (d, J = 9.0 Hz, 4H), 6.46 (dd, J = 8.0 Hz, 2.5 Hz, 2H), 4.01 (t, J = 6.8 Hz, 4H), 3.99-3.91 (m, 8H), 3.88 (t, J = 7.0 Hz, 4H), 3.73 (t, J = 6.5 Hz, 4H), 2.63-2.55 (m, 4H), 2.54-2.45 (m, 6H), 1.93-1.08 (m, 196H); ¹³C NMR (126 MHz, CDCl₃) δ 160.8, 160.6, 160.5, 160.4, 159.7, 156.6, 156.3, 147.0, 146.4, 146.3, 146.0, 138.4, 138.2, 136.6, 134.6, 134.0, 132.0, 131.8, 130.3, 129.6, 129.5, 129.0, 128.9, 127.5, 127.4, 127.1, 126.8, 126.2, 125.6, 125.4, 120.2, 119.4, 119.1, 114.7, 114.5, 113.6, 111.9, 111.6, 107.2, 101.1, 81.7, 79.1, 78.2, 73.6, 68.7, 68.11, 68.08, 68.0, 56.0, 44.2, 40.5, 34.4, 30.5, 30.0, 29.9, 29.74, 29.66, 29.60, 29.55, 29.5, 29.43, 29.41, 29.37, 29.1, 28.93, 26.90, 26.19, 26.16, 26.1, 26.0, 25.8, 25.7; IR(KBr) 3433, 3032, 2924, 2854, 2206, 2144, 1905, 1728, 1604, 1496, 1396, 1281, 1250, 1173, 1111, 1026, 1011, 833, 818, 748, 532 cm⁻¹; HR-MS (MALDI-TOF) Calcd for C₂₇₆H₃₂₅N₄O₁₀ ([M + H⁺]): 3853.4884. Found: 3853.5077.

Synthesis of Related Compounds.

Ring compound 11

A mixture of 6 (40 mg, 0.042 mmol), CuCl (0.42 g, 4.2 mmol) and CuCl₂ (70 mg, 0.52 mmol) in
dry pyridine (74 mL) was stirred at room temperature over 2 h. The color of the mixture changed from green to brown. The solution was stirred for 74 h and the solvent was removed in vacuo. Water was added to the dark green residue and the aqueous layer was extracted with CH₂Cl₂. The combined organic phase was washed with water, dried over Na₂SO₄, and concentrated. The residue was purified by silica gel column chromatography using CHCl₃ to afford **11** (33 mg, 0.035 mmol) in 85% yield as a white solid.

mp 186.0-188.1 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.41 (d, J = 8.5 Hz, 4H), 8.24 (d, J = 8.5 Hz, 2H), 8.07 (d, J = 8.5 Hz, 2H), 7.72 (s, 2H), 7.45 (dd, J = 7.5 Hz, 1.5 Hz, 2H), 7.29-7.22 (m, 2H), 7.08 (d, J = 8.5 Hz, 4H), 6.89-6.82 (m, 4H), 4.08-3.99 (m, 8H), 1.88-1.76 (m, 8H), 1.66-1.19 (m, 32H); ¹³C NMR (126 MHz, CDCl₃) δ 161.0, 160.5, 156.3, 146.0, 136.7, 134.3, 132.0, 130.3, 128.9, 127.5, 125.5, 120.3, 119.2, 114.8, 112.1, 111.9, 78.6, 78.0, 68.9, 68.1, 29.51, 29.48, 29.46, 29.4, 29.3, 29.2, 29.0, 26.0, 25.9; IR (KBr) 3433, 3070, 3039, 2924, 2854, 2206, 2144, 1597, 1489, 1450, 1396, 1281, 1250, 1173, 1119, 1041, 1026, 841, 795, 748, 571, 517 cm⁻¹; HR-MS (FAB) Calcd. For C₆₄H₇₁N₂O₄ ([M + H]+): 931.5408. Found: 931.5411.

Axle compound **12** (dimer of **2b**)

The reported procedure was generally followed to synthesize **12**.⁷ A solution of **2b** (42 mg, 0.038 mmol), piperidine (4.0 μL, 0.04 mmol) and Cu(OAc)₂·H₂O (1.0 mg, 5.0 μmol) in CH₂Cl₂ (0.1 mL) was stirred for 18 h. Water was added to the solution and the aqueous layer was extracted with CH₂Cl₂. The combined organic phase was washed with water, dried over Na₂SO₄, and concentrated. The residue was purified by silica gel column chromatography using hexane and CH₂Cl₂ (5/1 (v/v)) to afford **12** (37 mg, 0.017 mmol) in 86% yield as a colorless amorphous solid.

¹H NMR (500 MHz, CDCl₃) δ 7.50 (d, J = 8.0 Hz, 12H), 7.48 (d, J = 9.0 Hz, 12H), 7.41 (d, J = 8.5 Hz, 4H), 7.34 (d, J = 8.5 Hz, 12H), 7.24 (d, J = 8.0 Hz, 12H), 6.80 (d, J = 8.5 Hz, 4H), 3.92 (t, J = 6.5 Hz, 4H), 2.64-2.56 (m, 4H), 2.55-2.45 (m, 6H), 1.95-1.79 (m, 24H), 1.78-1.69 (m, 10H), 1.52-1.10 (m, 108H); ¹³C NMR (126 MHz, CDCl₃) δ 159.8, 147.0, 146.4, 138.4, 138.2, 134.0, 129.6, 127.2, 126.8, 126.2, 114.6, 113.7, 81.3, 72.9, 68.1, 56.0, 44.2, 40.5, 34.4, 30.5, 29.69, 29.67, 29.64, 29.58, 29.55, 29.5, 29.4, 29.1, 26.9, 26.2, 26.0, 25.7; IR (KBr) 3024, 2924, 2854, 1604, 1496, 1466, 1450, 1250, 810, 532 cm⁻¹; Anal. Calcd for C₁₆₆H₂₀₂O₂: C, 89.43; H, 9.13. Found: C, 89.25; H, 9.32.
**Figure 2-S1.** $^1$H NMR spectra of 12, 10d and 8b (500 MHz, CDCl$_3$).

**References**


SI-Chapter 3

General Procedure

Reagents were commercially available and used without further purification unless otherwise noted. Compounds 4,\(^1\) 7,\(^2\) 5b\(^3\) and 9\(^4\) were prepared by the reported procedures. NMR chemical shifts were reported in delta units (\(\delta\)) relative to chloroform-\(d\) (7.24 ppm for \(^1\)H NMR and 77.0 ppm for \(^{13}\)C NMR) or 1,1,2,2-tetrachloroethane-\(d\)_2 (73.8 ppm for \(^{13}\)C NMR). Multiplicity is indicated by s (singlet), d (doublet), t (triplet), m (multiplet) or br (broad). Coupling constants, \(J\), are reported in Hz. A recycling preparative HPLC, equipped with high-resolution GPC column(s) (exclusion limit: 1000 or 5000 MW), was used for the GPC separation. CHCl\(_3\) was used as the eluent (flow rate: 3.5 mL/min).

Preparation of Macrocyclic Phenanthrolines.

Alkyne 6a

\[
\text{CH}_3\chi_2\text{O} \quad \text{TMS}
\]

A reported procedure\(^5\) was generally followed to synthesize 6a. To a solution of 2-((trimethylsilyl)ethynyl)phenol (4, 1.3 g, 6.8 mmol) and PPh\(_3\) (2.7 g, 10 mmol) in dry THF (8.4 mL) was slowly added the solution of 6-chloro-1-hexanol (5a, 1.4 g, 10 mmol) and DEAD (4.6 mL, 40% in toluene) in dry THF (8.4 mL). After the mixture was refluxed for overnight, the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography using hexane and CH\(_2\)Cl\(_2\) (8:1 (v/v)) to afford 6a (1.9 g, 6.1 mmol) in 90% yield as a colorless oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.39 (dd, \(J = 7.6\) Hz, 1.6 Hz, 1H), 7.26-7.20 (m, 1H), 6.87-6.78 (m, 2H), 4.00 (t, \(J = 6.2\) Hz, 2H), 3.53 (t, \(J = 6.8\) Hz, 2H), 1.87-1.75 (m, 4H), 1.62-1.45 (m, 4H), 0.24 (s, 9H); \(^{13}\)C NMR (76 MHz, CDCl\(_3\)) \(\delta\) 160.1, 133.6, 129.9, 120.3, 112.7, 111.9, 101.3, 98.3, 68.2, 45.0, 32.6, 29.1, 26.6, 25.4, 0.04; IR (ATR) 2940, 2863, 2156, 1594, 1574, 1490, 1469, 1446, 1389, 1290, 1281, 1203, 1161, 1113, 1044, 969, 935, 699, 647 cm\(^{-1}\); Anal. Calcd for C\(_{17}\)H\(_{25}\)ClOSi: C, 66.10; H, 8.16. Found: C, 66.36; H, 8.29.
A reported procedure was generally followed to synthesize \(8a\). A mixture of 4,4’-(1,10-phenanthroline-2,9-diyl)diphenol HCl salt (7, 0.82 g, 2.1 mmol), \(6a\) (1.9 g, 6.2 mmol) and \(\text{K}_{2}\text{CO}_{3}\) (4.3 g, 31 mmol) in DMSO (23 mL) was stirred at 70 °C for 5 h. The solvent was removed \textit{in vacuo}, and \(\text{CH}_{2}\text{Cl}_{2}\) and \(\text{H}_{2}\text{O}\) was added to the residue. The organic layer and the aqueous layer were each separated, and the aqueous layer was extracted with \(\text{CH}_{2}\text{Cl}_{2}\). The combined organic layer was washed with water, dried over \(\text{Na}_{2}\text{SO}_{4}\), and concentrated. The crude product was purified by silica gel column chromatography using hexane and \(\text{CH}_{2}\text{Cl}_{2}\) (1:5 (v/v)) to afford \(8a\) (1.4 g, 1.8 mmol) in 84% yield as a pale yellow solid. mp 146.6-147.7 °C; \(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \(\delta\) 8.41 (d, \(J = 9.0\) Hz, 4H), 8.24 (d, \(J = 9.0\) Hz, 2H), 8.07 (d, \(J = 8.0\) Hz, 2H), 7.72 (s, 2H), 7.44 (dd, \(J = 6.0\) Hz, 1.5 Hz, 2H), 7.27 (td, \(J = 8.1\) Hz, 2.0 Hz, 2H), 7.08 (d, \(J = 8.5\) Hz, 4H), 6.90-6.84 (m, 4H), 4.11-4.02 (m, 8H), 3.24 (s, 2H), 1.95-1.80 (m, 8H); \(^{13}\text{C NMR}\) (126 MHz, CDCl\(_3\)) \(\delta\) 160.4, 160.1, 156.2, 145.9, 136.7, 134.0, 131.9, 130.1, 128.9, 127.4, 125.5, 120.2, 119.2, 114.7, 111.9, 111.6, 81.0, 80.1, 68.5, 67.8, 29.1, 28.9, 25.73, 25.70; \(\text{IR (ATR)}\) 3276, 2938, 2859, 1597, 1587, 1573, 1472, 1444, 1421, 1280, 1109, 1042, 1006, 994, 796, 659, 640, 626, 607, 577, 563, 511, 486 cm\(^{-1}\); HR-MS (ESI) Calcd for \(\text{C}_{52}\text{H}_{49}\text{N}_{2}\text{O}_{4}\) ([M + H\(^+\)]): 765.36868. Found: 765.36855.

Macrocyclic phenanthroline \(1a\)

To a mixture of \(8a\) (0.16 g, 0.21 mmol), \(\text{CuCl}\) (2.1 g, 21 mmol) and \(\text{CuCl}_2\) (0.35 g, 2.6 mmol) was added pyridine (432 mL), and the mixture was stirred at room temperature. After 3 days, the solvent was removed \textit{in vacuo}. \(\text{CH}_{2}\text{Cl}_{2}\) and 2 M HCl was added to the residue, and the organic layer and the aqueous layer were each separated. After the extraction of the aqueous layer with \(\text{CH}_{2}\text{Cl}_{2}\), the combined organic layer was washed with water, and dried over \(\text{Na}_{2}\text{SO}_{4}\). After the solvent was removed \textit{in vacuo}, the residue was dissolved in \(\text{CH}_{2}\text{Cl}_{2}\) (6 mL) and \(\text{CH}_3\text{CN}\) (28 mL). To the
solution was added NH₃ aq. (30% solution, 24 mL), and the mixture was stirred at room temperature for overnight. The white precipitate was filtered over paper and washed with water. The white solid was dried under reduced pressure (solid A). The filtrate was put into a separating funnel, and the aqueous layer and the organic layer were each separated. The aqueous layer was extracted with CH₂Cl₂. The combined organic layer was washed with water, and dried over Na₂SO₄. After the solvent was removed in vacuo, the residue was combined with the solid A, and purified by silica gel column chromatography using CHCl₃ to afford 1a (0.087 g, 0.11 mmol) in 55% yield as a pale yellow solid.

mp 247.6-248.3 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.43 (d, J = 9.0 Hz, 4H), 8.23 (d, J = 8.5 Hz, 2H), 8.06 (d, J = 8.5 Hz, 2H), 7.72 (s, 2H), 7.48 (dd, J = 8.0 Hz, 1.5 Hz, 2H), 7.29-7.22 (m, 2H), 7.10 (d, J = 8.5 Hz, 4H), 6.88-6.84 (m, 4H), 4.12 (t, J = 7.0 Hz, 4H), 4.08 (t, J = 7.0 Hz, 4H), 1.97-1.84 (m, 8H), 1.65-1.52 (m, 8H); ¹³C NMR (126 MHz, C₂D₂Cl₄) δ 160.5, 160.2, 155.9, 145.7, 136.8, 134.6, 131.6, 130.7, 128.9, 127.3, 125.49, 120.45, 119.0, 115.0, 112.1, 111.1, 79.0, 77.7, 68.7, 67.8, 28.9, 28.6, 25.5, 25.2; IR (ATR) 3035, 2942, 2871, 2857, 1610, 1595, 1582, 1571, 1483, 1446, 1263, 1244, 1173, 1145, 1117, 1049, 1014, 971, 837, 796, 742, 640, 629, 572, 544, 510, 481 cm⁻¹; HR-MS (ESI) Calcd for C₅₂H₄₇N₂O₄ ([M + H]+): 763.35303. Found: 763.35159.

Alkyne 6b

A reported procedure⁵ was generally followed to synthesize 6b. To a solution of 4 (2.5 g, 13 mmol) and PPh₃ (5.2 g, 20 mmol) in dry THF (16 mL) was slowly added the solution of 5b (3.3 g, 20 mmol) and DEAD (9.1 mL, 40% in toluene) in dry THF (16 mL). After the mixture was refluxed for overnight, the solvent was removed in vacuo. The crude product was purified by silica gel column chromatography using hexane and CH₂Cl₂ (2:1 (v/v)) to afford 6b (3.8 g, 11 mmol) in 86% yield as a colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 7.41 (dd, J = 7.7 Hz, 1.7 Hz, 1H), 7.29-7.19 (m, 1H), 6.92-6.80 (m, 2H), 4.20-4.14 (m, 2H), 4.00-3.90 (m, 4H), 3.48 (t, J = 6.2 Hz, 2H), 0.23 (s, 9H); ¹³C-NMR (76 MHz, CDCl₃) δ 159.5, 133.8, 129.8, 120.7, 112.7, 112.1, 101.3, 98.3, 71.7, 69.5, 68.7, 30.6, 0.01; IR (ATR) 2957, 2898, 2872, 2156, 1594, 1574, 1489, 1444, 1281, 1249, 1203, 1162, 1131, 1114, 1044, 1021, 928, 861, 840, 751, 699, 666, 645, 573, 490 cm⁻¹; Anal. Calcd for C₁₅H₂₁BrO₂Si: C, 52.78; H, 6.20. Found: C, 52.81; H, 6.18.
Diyne 8b

A reported procedure was generally followed to synthesize 8b. A mixture of 4,4’-(1,10-phenanthroline-2,9-diyl)diphenol HCl salt (7, 0.29 g, 0.72 mmol), 6b (0.74 g, 2.2 mmol) and K₂CO₃ (1.5 g, 11 mmol) in DMSO (8.5 mL) was stirred at 70 °C for 5.5 h. The solvent was removed in vacuo, and CH₂Cl₂ and H₂O was added to the residue. The organic layer and the aqueous layer were each separated, and the aqueous layer was extracted with CH₂Cl₂. The combined organic layer was washed with water, dried over Na₂SO₄, and concentrated. The crude product was purified by silica gel column chromatography using hexane and CH₂Cl₂ (1:4 (v/v)) to afford 8b (0.47 g, 0.64 mmol) in 89% yield as a yellow amorphous solid.

¹H NMR (300 MHz, CDCl₃) δ 8.40 (d, J = 9.0 Hz, 4H), 8.24 (d, J = 8.7 Hz, 2H), 8.06 (d, J = 8.7 Hz, 2H), 7.73 (s, 2H), 7.45 (dd, J = 7.5 Hz, 1.5 Hz, 2H), 7.35-7.21 (m, 2H), 7.11 (d, J = 8.7 Hz, 4H), 6.95-6.85 (m, 8H), 4.32-4.19 (m, 8H), 4.10-3.95 (m, 8H), 3.24 (s, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 159.8, 159.6, 155.7, 145.5, 136.5, 133.8, 131.9, 129.9, 128.6, 127.1, 125.3, 120.4, 118.9, 114.6, 112.0, 111.5, 81.2, 79.9, 69.8, 69.33, 68.32, 67.2; IR (ATR) 3273, 3068, 3038, 2925, 2872, 1598, 1588, 1574, 1486, 1442, 1420, 1280, 1245, 1174, 1130, 1111, 1052, 920, 836, 795, 746, 666, 638, 627, 605, 581, 570, 511 cm⁻¹; HR-MS (ESI) Calcd for C₄₈H₄₁N₂O₆ ([M + H]⁺): 741.29591; Found: 741.29615.

Macrocyclic phenanthroline 1b

To a mixture of 8b (0.2 g, 0.27 mmol), CuCl (2.7 g, 27 mmol) and CuCl₂ (0.44 g, 3.2 mmol) was added pyridine (540 mL), and the mixture was stirred at room temperature. After 3 days, the solvent was removed in vacuo. CH₂Cl₂ and 2M HCl was added to the residue, and the organic layer and the aqueous layer were each separated. After the extraction of the aqueous layer with CH₂Cl₂, the combined organic layer was washed with water, and dried over Na₂SO₄. After the solvent was removed in vacuo, the residue was dissolved in CH₂Cl₂ (20 mL) and CH₃CN (47 mL). To the
solution was added NH₃ aq. (30% solution, 52 mL), and the mixture was stirred at room temperature until the color of the organic layer changed from dark brown to yellow (3 days). The organic layer and the aqueous layer were each separated, and the aqueous layer was extracted with CH₂Cl₂. The combined organic layer was washed with water, and dried over Na₂SO₄. After the solvent was removed in vacuo, the residue was purified by silica gel column chromatography using CHCl₃ to afford 1b (0.14 g, 0.19 mmol) in 71% yield as a pale yellow amorphous solid.

1H NMR (500 MHz, CDCl₃) δ 8.41 (d, J = 9.0 Hz, 4H), 8.23 (d, J = 8.5 Hz, 2H), 8.05 (d, J = 8.5 Hz, 2H), 7.71 (s, 2H), 7.48 (dd, J = 7.5 Hz, 1.5 Hz, 2H), 7.26-7.19 (m, 2H), 7.13 (d, J = 9.0 Hz, 4H), 6.88 (d, J = 8.0 Hz, 2H), 6.85 (td, J = 7.5 Hz, 1.5 Hz, 2H), 4.38-4.33 (m, 4H), 4.28-4.22 (m, 4H), 4.11-4.06 (m, 4H), 4.04-3.99 (m, 4H); 13C NMR (126 MHz, CDCl₃) δ 160.5, 160.0, 156.0, 145.9, 136.6, 134.5, 132.2, 130.6, 128.9, 127.3, 125.4, 120.9, 118.9, 115.1, 112.2, 111.5, 78.9, 78.0, 70.2, 69.8, 68.8, 67.8; IR (ATR) 3068, 3036, 2926, 2872, 1600, 1586, 1573, 1485, 1442, 1420, 1280, 1247, 1173, 1133, 1115, 1054, 923, 838, 796, 746, 513 cm⁻¹; HR-MS (ESI) Calcd for C₄₈H₃₉N₂O₆ ([M + H]+): 739.28026. Found: 739.28032.

**Synthesis of [2]Rotaxanes.**

**Copper complex 1a-CuI**

A reported procedure⁷ was generally followed to synthesize 1a-CuI. To a suspension of 1a (0.22 g, 0.29 mmol) in CH₂Cl₂ (29 mL) and CH₃CN (5.7 mL) was added CuI (55 mg, 0.066 mmol), and the mixture was stirred at room temperature for 2 h. The solvent was removed in vacuo, and the residue was purified by recrystallization using (CH₂Cl₂) and hexane to afford 1a-CuI (0.21 g, 0.22 mmol) in 76% yield as a pale brown solid.

mp 218.4-218.8 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.42 (d, J = 8.5 Hz, 2H), 8.17-8.03 (m, 6H), 7.88 (s, 2H), 7.47 (dd, J = 7.5 Hz, 1.5 Hz, 2H), 7.29-7.22 (m, 2H), 7.10 (d, J = 8.5 Hz, 4H), 6.90-6.82 (m, 4H), 4.16-4.03 (m, 8H), 1.98-1.82 (m, 8H), 1.64-1.45 (m, 8H); ¹³C NMR (151 MHz, C₂D₂Cl₄) δ 160.8, 160.5, 157.7, 143.6, 137.8, 134.6, 131.0, 130.6, 130.1, 127.1, 125.7, 124.0, 120.3, 114.8, 112.1, 111.2, 79.1, 77.9, 68.8, 68.1, 28.8, 28.7, 25.6, 25.2; IR (ATR) 3071, 3038, 2942, 2907, 2865, 1604, 1582, 1490, 1478, 1446, 1421, 1392, 1362, 1331, 1279, 1241, 1176, 1165, 1124, 1115, 1071, 1015, 930, 853, 833, 786, 753, 739, 728, 649, 639, 602, 572, 535, 515, 500, 487, 471, 445 cm⁻¹; HR-MS (ESI) Calcd for C₅₂H₄₆N₂O₄₆₃Cu ([M - I]+): 825.27481. Found: 825.27617.
Copper complex 1b-CuI

To a solution of 1b (0.11 g, 0.15 mmol) in CH$_2$Cl$_2$ (7.5 mL) and CH$_3$CN (3.1 mL) was added CuI (29 mg, 0.15 mmol), and the mixture was stirred at room temperature for 1 h. the solvent was removed in vacuo, and the residue was passed through short silica gel column chromatography using CH$_2$Cl$_2$ to afford 1b-CuI (0.14 g, 0.15 mmol) in quantitative yield as a red amorphous solid.  

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.43 (d, $J$ = 8.5 Hz, 2H), 8.07 (d, $J$ = 8.0 Hz, 2H), 8.03 (d, $J$ = 8.5 Hz, 4H), 7.88 (s, 2H), 7.45 (dd, $J$ = 7.3 Hz, 1.8 Hz, 2H), 7.21 (td, $J$ = 8.1 Hz, 1.7 Hz, 2H), 7.11 (d, $J$ = 9.5 Hz, 4H), 6.91 (d, $J$ = 8.0 Hz, 2H), 6.84 (t, $J$ = 7.5 Hz, 2H), 4.34 (t, $J$ = 4.8 Hz, 4H), 4.27 (t, $J$ = 5.0 Hz, 4H), 4.06-4.01 (m, 4H), 3.98 (t, $J$ = 5.0 Hz, 4H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 160.4, 160.0, 157.0 (br), 143.1 (br), 137.8 (br), 134.4, 130.7 (br), 130.4, 130.2 (br), 126.9, 125.6, 123.4 (br), 120.7, 115.0, 112.4, 111.4, 79.0, 78.1, 69.5, 69.4, 68.5, 67.4; IR (ATR) 3063, 2924, 2871, 1603, 1583, 1573, 1485, 1442, 1420, 1279, 1246, 1174, 1112, 1047, 919, 858, 832, 796, 745, 667, 647, 636, 580, 560, 515, 486 cm$^{-1}$; HR-MS (ESI) Calcd for C$_{48}$H$_{38}$N$_2$O$_6^{63}$Cu ([M - I]$^+$): 801.20204. Found: 801.20121

[2]Rotaxane 2a

A solution of 1a-CuI (19 mg, 0.02 mmol), 9 (46 mg, 0.05 mmol), K$_2$CO$_3$ (11 mg, 0.076 mmol) and I$_2$ (6.6 mg, 0.026 mmol) in dry (CHCl$_3$)$_2$ (1.0 mL) was stirred at 80 °C for 2 days, and K$_2$CO$_3$ (11 mg, 0.076 mmol) and I$_2$ (6.6 mg, 0.026 mmol) were added to the solution. After stirring at 80 °C for overnight, the solvent was removed in vacuo. The residue was dissolved in CH$_2$Cl$_2$ (2.5 mL) and CH$_3$CN (3.5 mL), and NH$_3$ aq. (30% solution, 1.7 mL) was added to the solution. After stirring at room temperature for overnight, CH$_2$Cl$_2$ and H$_2$O was added to the mixture. The organic layer and the aqueous layer were each separated, and the aqueous layer was extracted with CH$_2$Cl$_2$.  

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The combined organic layer was washed with water, and dried over Na₂SO₄. After the solvent was removed in vacuo, and the residue was purified by silica gel column chromatography using hexane and CH₂Cl₂ (1:1 (v/v)) and GPC using CHCl₃ to afford 2a (23 mg, 8.7 μmol) in 43% yield as a pale yellow amorphous solid.

\[ \text{1H NMR (500 MHz, CDCl₃) } \delta 8.48 \ (d, \ J = 9.5, 4H), 8.17 \ (d, \ J = 8.0 \ Hz, 2H), 8.01 \ (d, \ J = 8.5 \ Hz, 2H), 7.67 \ (s, 2H), 7.53-7.43 \ (m, 26H), 7.42 \ (d, \ J = 9.0 \ Hz, 4H), 7.31 \ (d, \ J = 8.0 \ Hz, 12H), 7.26-7.17 \ (m, 14H), 7.08 \ (d, \ J = 9.0 \ Hz, 4H), 6.81 \ (t, \ J = 7.3 \ Hz, 2H), 6.76 \ (d, \ J = 8.5 \ Hz, 2H), 6.71 \ (d, \ J = 9.0 \ Hz, 4H), 3.91 \ (t, \ J = 7.3 \ Hz, 4H), 3.86 \ (t, \ J = 7.5 \ Hz, 4H), 3.78 \ (t, \ J = 6.5 \ Hz, 4H), 2.59-2.45 \ (m, 10H), 1.93-1.78 \ (m, 24H), 1.78-1.61 \ (m, 14H), 1.61-1.51 \ (m, 4H), 1.48-1.18 \ (m, 46H), 1.16-1.04 \ (m, 4H); \text{13C NMR (126 MHz, CDCl₃) } \delta 160.5, 160.3, 159.7, 156.0, 147.0, 146.3, 145.9, 138.3, 138.1, 136.5, 134.8, 134.1, 131.7, 130.4, 129.5, 129.0, 127.2, 127.1, 126.8, 126.2, 125.3, 120.3, 118.8, 114.8, 114.6, 113.5, 111.7, 111.4, 81.6, 79.1, 78.0, 73.2, 68.4, 67.93, 67.88, 55.9, 44.2, 40.3, 34.4, 30.4, 29.1, 29.0, 28.8, 26.9, 26.1, 25.8, 25.7, 25.2; \text{IR (ATR) } \text{3026, 2921, 2850, 1602, 1489, 1281, 1243, 1169, 1004, 832, 810, 746, 524 cm}^{-1}; \text{HR-MS (ESI) Calcd for C}_{190}H_{193}N_{2}O_{6} ([M + H]+): 2598.48531. Found: 2598.48104.\]

[2] Rotaxane 2b

A solution of 1b-CuI (19 mg, 0.02 mmol), 9 (46 mg, 0.05 mmol), K₂CO₃ (11 mg, 0.076 mmol) and I₂ (6.6 mg, 0.026 mmol) in (CH₂Cl₂) (1.0 mL) was stirred at 80 °C for 2 days, and K₂CO₃ (11 mg, 0.076 mmol) and I₂ (6.6 mg, 0.026 mmol) were added to the mixture. After stirring at 80 °C for overnight, the residue was dissolved in CH₂Cl₂ (1.5 mL) and CH₃CN (3.5 mL), and NH₃ aq., (30% solution, 1.7 mL) was added to the solution. After stirring at room temperature for overnight, CH₂Cl₂ and H₂O was added to the resulting solution. The organic layer and the aqueous layer were each separated, and the aqueous layer was extracted with CH₂Cl₂. The combined organic layer was washed with water, and dried over Na₂SO₄. After the solvent was removed in vacuo, and the residue was purified by silica gel column chromatography using hexane and CH₂Cl₂ (1:2 (v/v)) and GPC using CHCl₃ to afford 2b (24 mg, 9.2 μmol) in 46% yield as a yellow amorphous solid.

\[ \text{1H NMR (500 MHz, CDCl₃) } \delta 8.40 \ (d, \ J = 9.0 \ Hz, 4H), 8.17 \ (d, \ J = 8.5 \ Hz, 2H), 7.97 \ (d, \ J = 8.5 \ Hz, 2H), 7.69 \ (s, 2H), 7.52-7.40 \ (m, 26H), 7.38 \ (d, \ J = 9.5 \ Hz, 4H), 7.29 \ (d, \ J = 8.5 \ Hz, 12H), 7.26-7.15 \ (m, 14H), 7.00 \ (d, \ J = 9.5 \ Hz, 4H), 6.84-6.75 \ (m, 8H), 4.09 \ (t, \ J = 5.5 \ Hz, 4H), 4.00 \ (t, \ J = 5.3} \text{ cm}^{-1}; \text{HR-MS (ESI) Calcd for C}_{190}H_{193}N_{2}O_{6} ([M + H]+): 2598.48531. Found: 2598.48104.\]
Hz, 4H), 3.82 (t, J = 6.8 Hz, 4H), 3.79-3.73 (m, 8H), 2.57-2.44 (m, 10H), 1.94-1.78 (m, 24H), 1.78-1.69 (m, 6H), 1.63-1.57 (m, 4H), 1.48-1.33 (m, 24H), 1.33-1.18 (m, 14H), 1.13-1.03 (m, 4H); 13C
NMR (126 MHz, CDCl3) δ 160.3, 159.9, 159.8, 156.1, 147.0, 146.3, 145.9, 138.3, 138.1, 136.5, 136.1, 134.9, 134.1, 132.3, 130.5, 129.5, 128.9, 127.3, 127.1, 126.8, 126.2, 125.4, 120.7, 119.0, 114.9, 114.7, 113.5, 112.0, 111.4, 81.5, 79.0, 78.1, 73.1, 69.5, 69.2, 68.0, 67.8, 67.1, 55.9, 44.2, 40.3, 34.4, 30.2, 29.2, 26.9, 26.1, 25.9, 25.7; IR (ATR) 3026, 2921, 2848, 1600, 1445, 1281, 1169, 1113, 1051, 832, 779, 529 cm⁻¹; HR-MS (ESI) Calcd for C₁₈₆H₁₈₅N₂O₈ ([M + H]⁺): 2574.41254. Found: 2574.40830.

Synthesis of Rotacatenanes.
Tetrahedral Cu(I) complex 10a

A reported procedure⁶ was generally followed to synthesize 10a. To a solution of [Cu(CH₃CN)₄]PF₆ (8.8 mg, 0.024 mmol) in dry CH₃CN (3.4 mL) was added a solution of 2a (61 mg, 0.024 mmol) in CH₂Cl₂ (7.3 mL), and the mixture was stirred for 3 h at room temperature. To the mixture was added a solution of 8b (17 mg, 0.024 mmol) in CH₂Cl₂ (7.3 mL), and the mixture was stirred for 1 h at room temperature. After the solvent was removed in vacuo, the residue was purified by silica gel column chromatography using CH₂Cl₂ to afford 10a (67 mg, 0.019 mmol) in 79% yield as a brown amorphous solid.

¹H NMR (500 MHz, CDCl3) δ 8.40 (d, J = 8.5 Hz, 2H), 8.00 (d, J = 8.5 Hz, 2H), 7.92 (s, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 7.54 (s, 2H), 7.52-7.41 (m, 28H), 7.31 (d, J = 8.5 Hz, 4H), 7.31-7.21 (m, 20H), 7.19 (d, J = 9.0 Hz, 2H), 6.91-6.84 (m, 4H), 5.97 (d, J = 9.0 Hz, 4H), 4.24 (t, J = 4.8 Hz, 4H), 3.96-3.88 (m, 8H), 3.88-3.80 (m, 8H), 3.76-3.69 (m, 4H), 3.47 (t, J = 6.3 Hz, 4H), 3.24 (s, 2H), 2.66-2.56 (m, 4H), 2.55-2.44 (m, 6H), 1.92-1.70 (m, 34H), 1.69-1.62 (m, 4H), 1.62-1.51 (m, 4H), 1.47-1.12 (m, 50H); ¹³C NMR (126 MHz, CDCl3) δ 160.4, 160.0, 159.6, 159.4, 159.3, 156.4, 156.2, 147.1, 146.2, 143.3, 143.2, 138.4, 138.0, 137.3, 136.7, 135.2, 134.1, 133.8, 131.6, 131.3, 130.6, 130.3, 129.5, 129.0, 128.9, 127.9, 127.5, 127.2, 126.7, 126.3, 126.2, 125.8, 124.3, 124.3, 120.8, 120.4, 114.5, 113.3, 113.1, 112.8, 112.4, 111.8,
Tetrahedral Cu(I) complex 10b

A reported procedure was generally followed to synthesize 10b. To a solution of [Cu(CH3CN)4]PF6 (10 mg, 0.027 mmol) in CH3CN (4.0 mL) was added a solution of 2b (70 mg, 0.027 mmol) in CH2Cl2 (8.4 mL), and the mixture was stirred for 3 h at room temperature. To the mixture was added a solution of 8a (21 mg, 0.027 mmol) in CH2Cl2 (8.4 mL), and the mixture was stirred for 1 h at room temperature. After the solvent was removed in vacuo, the residue was purified by silica gel column chromatography using CH2Cl2 and AcOEt (40:1 (v/v)) to afford 10b (67 mg, 0.019 mmol) in 70% yield as a dark red amorphous solid.

1H NMR (500 MHz, CDCl3) δ 8.37 (d, \( J = 8.5 \) Hz, 2H), 7.91 (d, \( J = 9.0 \) Hz, 2H), 7.86 (s, 2H), 7.72 (d, \( J = 8.5 \) Hz, 2H), 7.53 (s, 2H), 7.52-7.37 (m, 30H), 7.35-7.18 (m, 32H), 7.08 (d, \( J = 8.5 \) Hz, 4H), 6.93 (d, \( J = 8.5 \) Hz, 2H), 6.90-6.82 (m, 10H), 6.34 (d, \( J = 8.5 \) Hz, 4H), 6.08 (d, \( J = 8.5 \) Hz, 4H), 5.99 (d, \( J = 8.5 \) Hz, 4H), 4.18 (t, \( J = 5.3 \) Hz, 4H), 4.03 (t, \( J = 6.3 \) Hz, 4H), 3.86 (t, \( J = 5.0 \) Hz, 4H), 3.75-3.66 (m, 8H), 3.62 (t, \( J = 6.8 \) Hz, 4H), 3.56 (t, \( J = 6.3 \) Hz, 4H), 3.20 (s, 2H), 2.58-2.45 (m, 10H), 1.93-1.78 (m, 28H), 1.77-1.69 (m, 6H), 1.69-1.60 (m, 4H), 1.49-1.04 (m, 50H); 13C NMR (126 MHz, CDCl3) δ 160.5, 160.2, 159.4, 159.2, 158.9, 156.9, 155.9, 147.1, 146.2, 143.4, 143.3, 138.4, 138.1, 137.3, 137.0, 135.2, 134.0, 133.6, 131.9, 131.7, 130.7, 130.3, 129.5, 128.8, 128.5, 128.0, 127.9, 127.2, 126.8, 126.6, 126.2, 126.1, 124.9, 124.1, 120.8, 120.3, 114.1, 113.3, 113.2, 113.0, 112.6, 112.1, 111.8, 111.6, 81.4, 81.0, 80.3, 79.2, 78.6, 73.7, 69.5, 69.4, 68.6, 68.1, 67.8, 67.7, 66.5, 55.9, 44.2, 40.4, 34.4, 30.2, 29.1, 28.94, 28.91, 26.86, 26.1, 25.8, 25.74, 25.71, 25.65; IR (ATR) 3287, 3028, 2922, 2849, 1602, 1489, 1445, 1281, 1245, 1170, 1110, 1044, 1004, 832, 811, 779, 748, 647, 636, 600, 556, 529, 512 cm\(^{-1}\); HR-MS (MALDI-TOF) Calcd for C\(_{238}H_{232}N_4O_{12}Cu\) ([M - PF\(_6\)]\(^+\)): 3400.6957. Found: 3400.6869.
Rotacatenane 3a

A mixture of 10a (67 mg, 0.019 mmol), CuCl (0.19 g, 1.9 mmol) and CuCl₂ (30 mg, 0.23 mmol) was dissolved in dry DMF (38 mL), and the solution was stirred for 3 days at room temperature. After the solvent was removed in vacuo, CH₂Cl₂ and H₂O was added to the residue. The organic layer and the aqueous layer was each separated, and the aqueous layer was extracted with CH₂Cl₂. The combined organic layer was washed with water, dried over Na₂SO₄, and concentrated. The residue was passed through a short silica gel column chromatography using CH₂Cl₂ and MeOH (10:1 (v/v)), and evaporation of the solvent gave the amorphous solid. The amorphous solid was dissolved in CH₂Cl₂ (3.8 mL), CH₃CN (3.8 mL) and H₂O (3.8 mL), and KCN (0.58 g) was added to the solution. After stirring at room temperature for overnight, CH₂Cl₂ and H₂O was added to the resulting solution. The organic layer and the aqueous layer were each separated, and the aqueous layer was extracted with CH₂Cl₂. The combined organic layer was washed with water, dried over Na₂SO₄, and concentrated. The residue was purified by silica gel column chromatography using CH₂Cl₂ and AcOEt (15:1 (v/v)) and GPC using CHCl₃ to afford 3a (39 mg, 0.012 mmol) in 62% yield as a yellow amorphous solid.

¹H NMR (500 MHz, CDCl₃) δ 8.53 (d, J = 8.5 Hz, 4H), 8.40 (d, J = 9.5 Hz, 4H), 8.16 (d, J = 8.5 Hz, 2H), 8.12 (d, J = 8.5 Hz, 2H), 8.04 (d, J = 8.5 Hz, 2H), 7.94 (d, J = 8.5 Hz, 2H), 7.64 (s, 2H), 7.63 (s, 2H), 7.50-7.40 (m, 28H), 7.33 (d, J = 8.5 Hz, 4H), 7.07 (t, J = 7.3 Hz, 2H), 7.01 (d, J = 9.0 Hz, 4H), 6.79-6.65 (m, 12H), 4.06 (t, J = 5.5 Hz, 4H), 3.97 (t, J = 5.3 Hz, 4H), 3.93 (t, J = 7.5 Hz, 4H), 3.81 (t, J = 6.5 Hz, 4H), 3.75 (t, J = 8.0 Hz, 4H), 3.71-3.63 (m, 8H), 2.57-2.44 (m, 10H), 1.92-1.78 (m, 24H), 1.77-1.48 (m, 18H), 1.47-1.15 (m, 46H), 1.14-1.04 (m, 4H); ¹³C NMR (126 MHz, CDCl₃) δ 160.5, 160.42, 160.38, 159.9, 159.6, 156.2, 156.1, 147.0, 146.3, 146.1, 146.0, 138.3, 138.1, 136.6, 136.4, 135.2, 134.9, 134.1, 132.3, 131.6, 130.43, 130.40, 129.6, 129.1, 129.0, 127.32, 127.25, 127.2, 126.8, 126.2, 125.4, 120.5, 120.0, 119.1, 118.9, 115.0, 114.9, 114.7, 113.4, 111.9, 111.4, 111.3, 111.2, 81.7, 79.6, 79.3, 78.3, 78.2, 73.3, 69.4, 69.0, 68.5, 68.2, 67.9, 67.7, 67.0, 55.9, 44.2, 40.3, 34.4, 30.2, 29.4, 29.3, 29.0, 26.9, 26.2, 26.1, 25.9, 25.7, 25.5; IR (ATR) 3026, 2922, 2849, 1600, 1587, 1574, 1487, 1445, 1280, 1244, 1171, 1113, 1048, 1004, 834, 812, 795, 747, 533, 523 cm⁻¹; HR-MS (MALDI-TOF) Calcd for C₂₃₈H₂₃₁N₄O₁₂ ([M + H]⁺): 3336.7583. Found: 3336.7358.
Rotacatenane 3b

A mixture of 10b (67 mg, 0.019 mmol), CuCl (0.19 g, 1.9 mmol) and CuCl2 (30 mg, 0.23 mmol) was dissolved in dry DMF (38 mL), and the solution was stirred for 3 days at room temperature. After the solvent was removed in vacuo, CH2Cl2 and H2O was added to the residue. The organic layer and the aqueous layer were each separated, and the aqueous layer was extracted with CH2Cl2. The combined organic layer was washed with water, dried over Na2SO4, and concentrated. The residue was passed through a short silica gel column chromatography using CH2Cl2 and MeOH (10:1 (v/v)), and evaporation of the solvent gave the amorphous solid. The amorphous solid was dissolved in CH2Cl2 (3.8 mL), CH3CN (3.8 mL) and H2O (3.8 mL), and KCN (0.58 g) was added to the solution. After stirring the solution at room temperature for overnight, CH2Cl2 and H2O was added to the resulting solution. The organic layer and the aqueous layer were each separated, and the aqueous layer was extracted with CH2Cl2. The combined organic layer was washed with water, dried over Na2SO4, and concentrated. The residue was purified by silica gel column chromatography using CH2Cl2 and AcOEt (20:1 (v/v)) and GPC using CHCl3 to afford 3b (45 mg, 0.013 mmol) in 71% yield as a yellow amorphous solid.

1H NMR (500 MHz, CDCl3) δ 8.46 (d, J = 8.5 Hz, 4H), 8.29 (d, J = 8.5 Hz, 4H), 8.19 (d, J = 8.5 Hz, 2H), 8.11 (d, J = 8.0 Hz, 2H), 7.99-7.93 (m, 4H), 7.69 (s, 2H), 7.61 (s, 2H), 7.47 (d, J = 8.0 Hz, 4H), 7.43 (d, J = 8.5 Hz, 12H), 7.39 (dd, J = 7.5 Hz, 2.0 Hz, 2H), 7.26 (d, J = 8.5 Hz, 12H), 7.24-7.18 (m, 16H), 7.15 (t, J = 7.9 Hz, 2H), 7.11 (d, J = 9.0 Hz, 4H), 7.09-7.01 (m, 6H), 6.79 (d, J = 8.5 Hz, 2H), 6.72 (t, J = 7.3 Hz, 2H), 6.68 (t, J = 7.5 Hz, 2H), 6.65 (d, J = 9.0 Hz, 2H), 6.51 (d, J = 8.5 Hz, 4H), 4.22-4.11 (m, 8H), 3.87 (t, J = 5.8 Hz, 4H), 3.84-3.73 (m, 12H), 3.67 (t, J = 7.0 Hz, 4H), 2.55-2.42 (m, 10H), 1.93-1.77 (m, 24H), 1.77-1.69 (m, 6H), 1.67-1.48 (m, 12H), 1.47-1.08 (m, 46H), 1.07-0.96 (m, 4H); 13C NMR (126 MHz, CDCl3) δ 160.5, 160.4, 160.2, 159.7, 159.5, 157.0, 155.9, 147.0, 146.4, 146.3, 145.9, 138.3, 138.1, 136.5, 136.4, 135.5, 134.8, 133.9, 132.6, 131.4, 130.5, 130.3, 129.5, 129.3, 128.8, 127.5, 127.1, 126.7, 126.23, 126.16, 125.6, 125.3, 120.7, 119.9, 119.8, 118.7, 115.0, 114.8, 114.4, 113.4, 111.8, 111.7, 111.4, 111.3, 81.9, 79.4, 79.3, 78.5, 78.2, 73.6, 69.3, 69.1, 68.5, 68.1, 67.9, 67.7, 66.6, 55.9, 44.2, 40.3, 34.4, 30.2, 29.2, 29.0, 28.8, 26.9, 26.1, 25.74, 25.69, 25.6, 25.2; IR (ATR) 3027, 2921, 2849, 1600, 1588, 1574, 1487, 1445, 1419, 1279, 1243, 1171, 1113, 1049, 1004, 833, 811, 796, 779, 746, 639, 562, 530, 485, 472 cm⁻¹;
HR-MS (MALDI-TOF) Calcd for C\textsubscript{238}H\textsubscript{231}N\textsubscript{4}O\textsubscript{12} ([M + H]\textsuperscript{+}): 3336.7583. Found: 3336.7535.

**Figure 3-S1.** \textsuperscript{1}H NMR spectra of 2b, 1b and 11\textsuperscript{8} (500 MHz, CDCl\textsubscript{3}).

**Figure 3-S2.** \textsuperscript{1}H NMR spectra of 3b, 2b and 1a (500 MHz, CDCl\textsubscript{3}).
References


500 MHz, CDCl₃
500 MHz CDCl₃

500 MHz, CDCl₃
500 MHz, CDCl₃
SI-Chapter 4

General Procedure

Reagents were commercially available and used without further purification unless otherwise noted. Macrocyclic phenanthrolines (1a and 1b),\(^1\) 4,4′-(1,10-phenanthroline-2,9-diyl)diphenol (3),\(^2\) 4′,4″,4‴″-(7-iodoheptane-1,1,1-triy)tris(4-cyclohexyl-1,1′-biphenyl) (5)\(^3\) and 2,9-bis(4-(prop-2-yn-1-yloxy)-phenyl)-1,10-phenanthroline (10)\(^4\), Macrocyclic phenanthroline-CuI complex (20)\(^5\) and alkyne (21)\(^3\) were prepared as reported. [2]Rotaxanes (7a, 7b and 7d) were prepared by the procedure for the synthesis of 3c, 3d and 3b described in SI-Chapter 2. Diyne (16) was prepared by the procedure for the synthesis of 6 described in SI-Chapter 2. 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), m (multiplet) or br (broad). Coupling constants, \(J\), are reported in Hz. A recycling preparative HPLC, equipped with high-resolution GPC column(s) (exclusion limit: 1000, 5000, or 30000 MW), was used for the GPC separation (eluent: chloroform). Preparative thin layer chromatography (PTLC) was performed using a Merck silica gel 60 plate.


General procedure was reported in the reference.\(^3\) A mixture of macrocyclic phenanthroline 1a (9.0 mg, 0.013 mmol) and [Cu(CH\(_3\)CN)\(_4\)]PF\(_6\) (4.8 mg, 0.013 mmol) in dry CH\(_2\)Cl\(_2\) (1.0 mL) was stirred at room temperature for 20 min (mixture A). The reaction mixture was added to a suspension of 3 (4.7 mg, 0.013 mmol) in dry CH\(_3\)CN (1.0 mL). A trace amount of mixture A in the flask was also added to the resulting mixture by using dry CH\(_2\)Cl\(_2\) (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, 0.026 mmol), Cs\(_2\)CO\(_3\) (17 mg, 0.052 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\(_3\)CN (2.0 mL), CH\(_2\)Cl\(_2\) (2.0 mL), H\(_2\)O (2.0 mL), and KCN (33 mg) were added to the residue. After stirring at room temperature for overnight, water and CH\(_2\)Cl\(_2\) were added to the mixture. The organic layer and the aqueous layer were each separated, and the aqueous layer was extracted with CH\(_2\)Cl\(_2\). The combined organic layer was washed with water, dried over Na\(_2\)SO\(_4\), and concentrated. The residue was purified by silica gel column
chromatography using hexane and CH$_2$Cl$_2$ (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. The analytical data were identical with those reported in the reference.$^3$

**Preparation of a [2]Rotaxane (7c).**

![Diagram of [2]Rotaxane (7c)](image)

The procedure for the synthesis of 3a-d which was described in SI-Chapter 2 was generally followed to synthesize 7c. A mixture of macrocyclic phenanthroline-CuI complex 20 (17 mg, 0.02 mmol), 21 (46 mg, 0.05 mmol), K$_2$CO$_3$ (10 mg, 0.075 mmol) and I$_2$ (6.3 mg, 0.025 mmol) in dry xylene (1.0 mL) under Ar atmosphere was stirred at 130 °C for 48 h. The solution was cooled to room temperature and CH$_2$Cl$_2$ (1.5 mL), CH$_3$CN (3.5 mL) and aqueous ammonia (30% solution, 1.7 mL) was added. After stirring at room temperature for overnight, the solution was extracted with CH$_2$Cl$_2$, dried over Na$_2$SO$_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography using hexane and CH$_2$Cl$_2$ (1/1 (v/v)) and GPC using CHCl$_3$ to afford 7c (35 mg, 0.014 mmol) in 70% yield as a colorless amorphous solid. The analytical data were identical with those reported in the reference.$^3$

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


![Diagram of [3]Rotaxane 9a](image)

A mixture of [2]rotaxane 7a (34 mg, 0.013 mmol) and [Cu(CH$_3$CN)$_4$]PF$_6$ (5.0 mg, 0.013 mmol)
in dry CH₂Cl₂ (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 CH₃CN (1.0 mL). A trace amount of mixture A in the flask was also added to the resulting mixture by using dry CH₂Cl₂ (2.0 mL). After stirring at room temperature for 1 h, the solvent was removed in vacuo and 5 (25 mg, 0.027 mmol), Cs₂CO₃ (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, CH₃CN (2.0 mL), CH₂Cl₂ (2.0 mL), H₂O (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 CH₂Cl₂ were added to the mixture, the organic layer and the aqueous layer were each separated and the aqueous layer was extracted with CH₂Cl₂. The combined organic layer was washed with water, dried over Na₂SO₄, and concentrated. The residue was purified by silica gel column chromatography using hexane and CH₂Cl₂ (1:1 (v/v)) and preparative thin-layer chromatography (PTLC) using CH₂Cl₂ and AcOEt (30:1 (v/v)) to afford 9a (19 mg, 4.1 μmol) in 31% yield as a colorless amorphous solid.

1H NMR (500 MHz, CDCl₃) 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);

13C NMR (126 MHz, CDCl₃) δ 160.6, 160.5, 160.4, 159.5, 156.7, 156.6, 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, 1802, 1598, 1447, 1447, 1271, 1173, 1005, 834, 813 cm⁻¹;


[3]Rotaxane 9b

A mixture of [2]rotaxane 7b (38 mg, 0.013 mmol) and [Cu(CH₃CN)₄]PF₆ (4.8 mg, 0.013 mmol) in dry CH₂Cl₂ (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 CH3CN (1.0 mL). A trace amount of mixture A in the flask was also added to the resulting mixture by using dry CH3Cl2 (1.5 mL). After stirring at room temperature for 1 h, the solvent was removed in vacuo and 5 (24 mg, 0.026 mmol), Cs2CO3 (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, CH3CN (2.0 mL), CH2Cl2 (2.0 mL), H2O (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 CH2Cl2 were added to the mixture, the organic layer and the aqueous layer were each separated and the aqueous layer was extracted with CH2Cl2. The combined organic layer was washed with water, dried over Na2SO4, and concentrated. The residue was purified by silica gel column chromatography using hexane and CH2Cl2 (1:1 (v/v)) and PTLC using CH2Cl2 and AcOEt (40:1 (v/v)) to afford 9b (12 mg, 2.5 μmol) in 20% yield as a pale yellow amorphous solid.

1H NMR (500 MHz, CDCl3) 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), 7.49–7.42 (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); 13C NMR (126 MHz, CDCl3) 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, 128.5, 127.5, 127.3, 127.14, 127.12, 126.8, 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, 73.6, 70.00, 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 C358H405N4O8 ([M + H]+): 4888.1402. Found: 4888.1459.

Preparation of 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 NaN3 (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 CH2Cl2 (4:1 (v/v)). Further purification of the product was carried out by flash column chromatography (silica gel) using hexane and CH2Cl2 (4:1 (v/v)) to afford 12 (0.31 g, 0.37 mmol) in 74% yield as a white amorphous powder.

1H NMR (300 MHz, CDCl3) δ 7.55–7.44 (12H, m), 7.34 (6H, d, J = 8.7 Hz), 7.28–7.20 (6H, m),

[2]Rotaxane 13a

To a solution of [Cu(CH3CN)4]PF6 (4.8 mg, 0.013 mmol) in dry CH3CN (2.0 mL) was added the solution of 1a (9.0 mg, 0.013 mmol) in dry CH2Cl2 (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 CH2Cl2 (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), CuSO4·5H2O (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, CH2Cl2 (2.0 mL), CH3CN (2.0 mL), H2O (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). CH2Cl2 was added to the solution, and the aqueous layer was extracted with CH2Cl2. The organic layer was washed with water, dried over Na2SO4, and concentrated. The residue was purified by silica gel column chromatography using CH2Cl2 and PTLC using CH2Cl2 and AcOEt (80/1 (v/v)) to afford 13a (23 mg, 8.3 μmol) in 63% yield as a pale yellow amorphous solid.

1H NMR (500 MHz, CDCl3) 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); 13C NMR (126 MHz, CDCl3) 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,
To a solution of [Cu(CH3CN)4]PF6 (4.8 mg, 0.013 mmol) in dry CH3CN (2.0 mL) was added the solution of 1b (8.3 mg, 0.013 mmol) in dry CH2Cl2 (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 CH2Cl2 (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), CuSO4·5H2O (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, CH2Cl2 (2.0 mL), CH3CN (2.0 mL), H2O (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). CH2Cl2 was added to the solution, and the aqueous layer was extracted with CH2Cl2. The organic layer was washed with water, dried over Na2SO4, and concentrated. The residue was purified by PTLC using CH2Cl2 and AcOEt (20/1 (v/v)) to afford 13b (27 mg, 9.8 μmol) in 76% yield as a pale yellow amorphous solid. 

1H NMR (500 MHz, CDCl3) 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), 3.65−3.58 (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); 13C NMR (126 MHz, CDCl3) 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 C194H202N10O6 ([M + 2H]2+): 1383.78989. Found: 1383.78987.

[3]Rotaxane 15a

To a solution of [Cu(CH3CN)4]PF6 (7.8 mg, 0.021 mmol) in dry CH3CN (1.2 mL) was added the solution of [2]rotaxane 7a (53 mg, 0.021 mmol) in dry CH2Cl2 (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 CH2Cl2 (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), CuSO4·5H2O (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, CH2Cl2 (2.5 mL), CH3CN (2.5 mL), H2O (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 CH2Cl2 were added to the suspension, the organic layer and the aqueous layer were each separated and the aqueous layer was extracted with CH2Cl2. The combined organic layer was washed with water, dried over Na2SO4, and concentrated. The residue was purified by silica gel column chromatography using CH2Cl2 and GPC using CHCl3 to afford 15a (57 mg, 0.012 mmol) in 59% yield as a pale yellow amorphous solid.

1H NMR (500 MHz, CDCl3) 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), 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); 13C NMR (126 MHz, CDCl3) 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 C336H355N10O8 ([M + H]+): 4657.7674. Found:
To a solution of [Cu(CH$_3$CN)$_4$]PF$_6$ (6.3 mg, 0.017 mmol) in dry CH$_3$CN (1.0 mL) was added a solution of [2]rotaxane 7b (50 mg, 0.017 mmol) in dry CH$_2$Cl$_2$ (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$_2$Cl$_2$ (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$_4$·5H$_2$O (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$_2$Cl$_2$ (2.0 mL), CH$_3$CN (2.0 mL), H$_2$O (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$_2$Cl$_2$ were added to the reaction mixture, the organic layer and the aqueous layer were each separated and the aqueous layer was extracted with CH$_2$Cl$_2$. The combined organic layer was washed with water, dried over Na$_2$SO$_4$, and concentrated. The residue was purified by silica gel column chromatography using CH$_2$Cl$_2$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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, 128.75, 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 [Cu(CH\(_3\)CN)\(_4\)]PF\(_6\) (7.7 mg, 0.021 mmol) in dry CH\(_3\)CN (1.2 mL) was added a solution of [2]rotaxane 7c (51 mg, 0.021 mmol) in dry CH\(_2\)Cl\(_2\) (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\(_2\)Cl\(_2\) (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\(_4\)·5H\(_2\)O (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\(_2\)Cl\(_2\) (2.5 mL), CH\(_3\)CN (2.5 mL), H\(_2\)O (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\(_2\)Cl\(_2\) were added to the reaction mixture, the organic layer and the aqueous layer were each separated and the aqueous layer was extracted with CH\(_2\)Cl\(_2\). The combined organic layer was washed with water, dried over Na\(_2\)SO\(_4\), and concentrated. The residue was purified by silica gel column chromatography using CH\(_2\)Cl\(_2\) 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\(_3\)) \(\delta 8.31–8.15\) (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\(_3\)) \(\delta 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, 138.2, 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 [Cu(CH$_3$CN)$_4$]PF$_6$ (7.5 mg, 0.020 mmol) in dry CH$_3$CN (1.2 mL) was added a solution of [2]rotaxane 7d (57 mg, 0.020 mmol) in dry CH$_2$Cl$_2$ (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$_2$Cl$_2$ (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$_4$·5H$_2$O (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$_2$Cl$_2$ (2.4 mL), CH$_3$CN (2.4 mL), H$_2$O (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$_2$Cl$_2$ were added to the reaction mixture, the organic layer and the aqueous layer were separated and the aqueous layer was extracted with CH$_2$Cl$_2$. The combined organic layer was washed with water, dried over Na$_2$SO$_4$, and concentrated. The residue was purified by silica gel column chromatography using CH$_2$Cl$_2$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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, 125.3, 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, 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.


To a solution of $[\text{Cu(CH$_3$CN)$_4$}]PF_6$ (7.0 mg, 0.019 mmol) in dry CH$_3$CN (1.1 mL) was added a solution of 2 rotaxane 7b (55 mg, 0.019 mmol) in dry CH$_2$Cl$_2$ (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$_2$Cl$_2$ (2.3 mL). After 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$_2$O (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$_2$Cl$_2$ (2.3 mL), CH$_3$CN (2.3 mL), H$_2$O (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$_2$Cl$_2$ were added to the reaction mixture, the organic layer and the aqueous layer were each separated and the aqueous layer was extracted with CH$_2$Cl$_2$. The combined organic layer was washed with water, dried over Na$_2$SO$_4$, and concentrated. The residue was purified by silica gel column chromatography (hexane/CH$_2$Cl$_2$ 1:1 (v/v) and CH$_2$Cl$_2$) and PTLC using CH$_2$Cl$_2$ 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$_3$) $\delta$ 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$_3$) $\delta$ 160.5, 160.4, 160.3, 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, 127.5, 127.5, 127.4, 127.1, 126.7, 126.7, 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, 68.0, 67.9, 67.9, 67.9.
To a solution of [Cu(CH$_3$CN)$_4$]PF$_6$ (7.5 mg, 0.020 mmol) in dry CH$_3$CN (1.2 mL) was added a solution of [2]rotaxane 7d (57 mg, 0.020 mmol) in dry CH$_2$Cl$_2$ (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$_2$Cl$_2$ (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$_2$O (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$_2$Cl$_2$ (2.4 mL), CH$_3$CN (2.4 mL), H$_2$O (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$_2$Cl$_2$ were added to the reaction mixture, the organic layer and the aqueous layer were each separated and the aqueous layer was extracted with CH$_2$Cl$_2$. The combined organic layer was washed with water, dried over Na$_2$SO$_4$, and concentrated. The residue was purified by silica gel column chromatography (hexane/CH$_2$Cl$_2$ 2:1 (v/v), CH$_2$Cl$_2$ and CH$_2$Cl$_2$/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, 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 C₃₉₄H₄₅₅N₁₀O₁₀ ([M + H]⁺): 5486.5397. Found: 5486.5500.

Unthreaded axle component 18

In the synthesis of 13a, 18 (6.3 mg, 3.0 μmol) was also obtained in 23% yield as a colorless amorphous solid. ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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 C₁₅₂H₁₆₀N₈O₂ ([M + 2H]²⁺): 1064.6326. Found: 1064.6322.

Unthreaded axle component 19

In the synthesis of 15f, 19 (40 mg, 0.015 mmol) was also obtained in 77% yield as a colorless amorphous solid; ¹H NMR (500 MHz, CDCl₃) 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$_8$O$_4$ ([M + 2H]$^{2+}$): 1310.83103. Found: 1310.83498.
500 MHz, CDCl₃
500 MHz, CDCl₃
500 MHz, CDCl₃
500 MHz, CDCl₃
500 MHz, CDCl₃
500 MHz, CDCl₃
500 MHz, CDCl₃
500 MHz, CDCl₃
500 MHz, CDCl₃
500 MHz, CDCl₃
500 MHz, CDCl₃

500 MHz, CDCl₃
500 MHz, CDCl₃

500 MHz, CDCl₃
Figure 4-S1. Partial $^1$H NMR spectra of 7a, 9a and unthreaded axle component 22$^3$ (500 MHz, CDCl$_3$).

Figure 4-S2. Partial $^1$H NMR spectra of 15d (600 MHz, DMSO-$d_6$/CDCl$_3$).
References


Publication List

1. Synthesis of rotacatenanes by the combination of Cu-mediated threading reaction and the template method: the dual role of one ligand


Publication Date (Web): October 24, 2013. DOI: 10.1039/C3CC47425A

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


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3. Sequence-Selective Synthesis of Rotacatenane Isomers


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