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Sequence-Selective Synthesis of Rotacatenane Isomers

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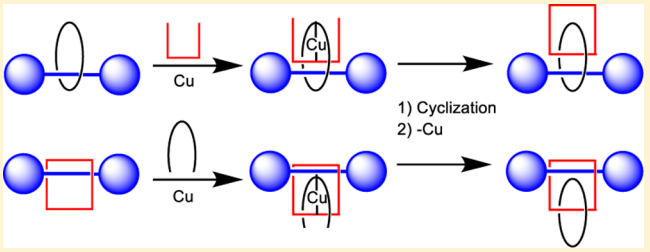
Supporting Information

ABSTRACT: Rotacatenane is an interlocked compound composed of two mechanically interlocked macrocyclic components, i.e., a [2]catenane, and one axle component. In this paper we describe the selective synthesis of isomeric rotacatenanes. Two [2]rotaxanes with different phenanthroline moieties were synthesized by the oxidative coupling of an alkyne with a bulky blocking group, which 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 rotacatenanes were distinguished by ^{1}H and ^{13}C NMR spectroscopy.



INTRODUCTION

Interlocked compounds composed of three or more components recently attracted great interest due to the remarkable progress in the synthesis of these complex compounds.[1−9] Some examples of the interlocked compounds with three components are depicted in Figure 1. A [3]rotaxane (type 1.2) is composed of two ring components and one axle component.[2] A rotacatenane is composed of two ring components and one axle component with a different connectivity, and it is an isomer of a [3]rotaxane (type 1.2).[5] A [3]catenane[7,8] is composed of three ring components.

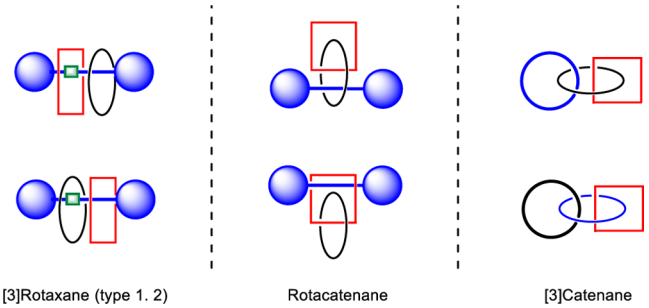


Figure 1. Structures and sequential isomers of interlocked compounds with three components.

In the chemistry of interlocked compounds with three or more components, a unique issue related to the connectivity of the components would arise (Figure 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.[9] 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. As is the case for the peptides and DNA, where the connectivity of the monomeric fragment (amino acid or nucleotide) determines the function of the molecule, the "mechanical" connectivity of the components would correlate with the chemical or physical properties of the interlocked compounds. Accordingly, the chemistry related to the sequential isomerism of interlocked compounds, which is a very interesting phenomenon, remains to be explored.

The first synthesis of rotacatenane was reported by Stoddart and co-workers in 1999,[5a] and the study related to the application of the rotacatenane to a molecular device was subsequently carried out.[5b] The strong nonbonding 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.[5c] A [2]rotaxane, which was prepared by oxidative coupling of an alkyne utilizing the catalytic activity of a macrocyclic phenanthroline–CuI complex,[10a,f,h,i,11] 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 the Cu(I) ion resulted in the synthesis of the rotacatenane.[7,12,13] The combination of the Cu-mediated

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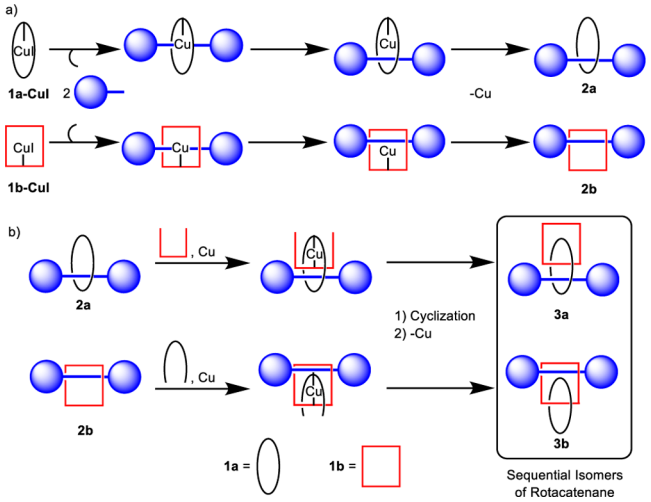
threading reaction and the metal-template method turned out to be an efficient strategy for the synthesis of rotacatenane.

We envisioned that the sequence-selective synthesis of rotacatenane isomers could be realized by applying the synthetic strategy we established (Scheme 1).[5c] Two different

Scheme 1. A Strategy for the Synthesis of Rotacatenane Isomers

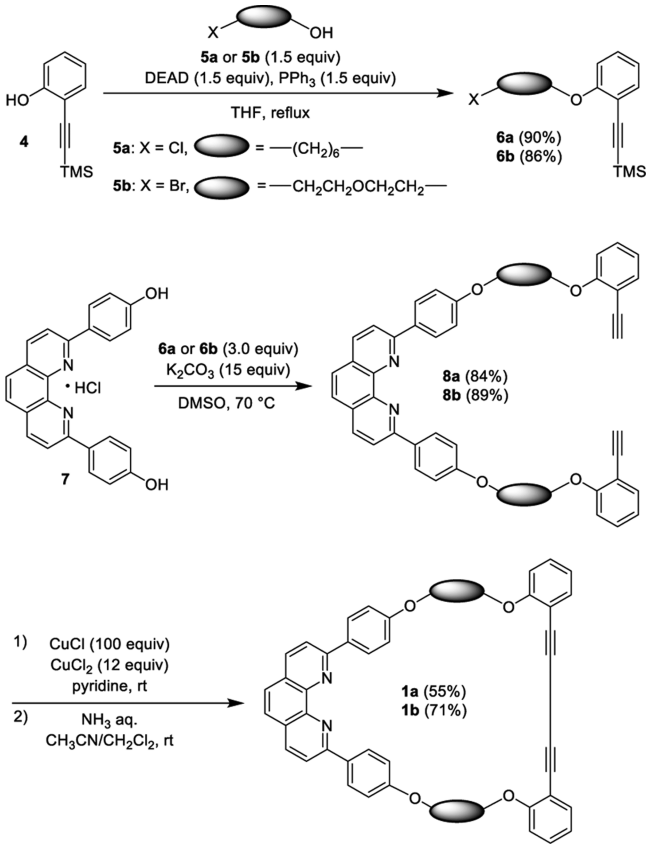


macrocyclic phenanthrolines **1a,b** are designed, and [2]-rotaxane **2a** and **2b** would be prepared by the oxidative coupling of an alkyne using **1a-CuI** and **1b-CuI**, respectively (Scheme 1a). Rotacatenane **3a** would be synthesized by the installation of a different ring component in **2a** using the Cu(I) ion as template (Scheme 1b). Another rotacatenane **3b** would be also synthesized from **2b**. If we could design two ring compounds which would be used as the ligand in Scheme 1a and install the same cyclic structure in the late-stage cyclization (Scheme 1b), it is possible to install two different ring components in a different sequence to a rotacatenane. Two rotacatenanes (**3a,b**) are sequential isomers: the structures of the three components of **3a,b** are identical, and the isomerism was induced by the difference in the connectivity of the components. In this paper, we report the sequence-selective synthesis of the isomeric rotacatenanes.

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 2. Mitsunobu reaction of 2-((trimethylsilyl)ethynyl)phenol (**4**)[14a] with 6-chloro-1-hexanol (**5a**) gave **6a**,[14b] and **6a** was reacted with a phenanthroline derivative (**7**)[11a,12c,15] under basic conditions to yield **8a**. The cyclization of **8a** was carried out in the presence of CuCl and $CuCl_2$.[5c,7] The macrocyclic phenanthroline **1a** was isolated in 55% yield when the reaction was carried out under highly diluted conditions: 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 four 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,b**) would be employed as the precursor for the late-stage cyclization.

Scheme 2. Preparation of Macrocyclic Phenanthrolines



The synthesis of [2]rotaxanes is described in Scheme 3. The macrocyclic phenanthroline−Cu complex **1a-CuI** was synthesized by the reaction of **1a** with CuI,[11a] and **1a-CuI** was reacted with an alkyne (**9**) in the presence of K_2CO_3 and I_2 at 80 °C for 3 days.[3e,5c,10a,f,h,i,11b] The mixture was treated with aqueous ammonia to remove the Cu ion from the rotaxane−Cu complex.[16] The formation of the [2]rotaxane was sluggish when the reaction was carried out in xylene[3e,5c,10h,i,11b] or THF/toluene.[17] We assume that the low solubility of **1a-CuI** in these solvents was responsible for the observed low rate of the reaction. We found that **1a-CuI** has better solubility in 1,1,2,2-tetrachloroethane.[18] 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,b** in hand, rotacatenane isomers were synthesized by the introduction of the second mechanical bond using Sauvage and co-worker's $Cu(phen)_2$ template approach.[7,12] The results are summarized in Scheme 4. [2]Rotaxane **2a** was reacted with $[Cu(CH_3CN)_4]PF_6$ 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 a stable red solid in 79% yield. As we expected,[3f,5c] the tetrahedral complex **10a** could be employed as a stable substrate, which does not undergo facile dissociation, under the conditions required for further transformation. The cyclization of the acyclic phenanthroline moiety of **10a** was carried out in the presence of CuCl and $CuCl_2$[5c,7,8a,b,19] at room

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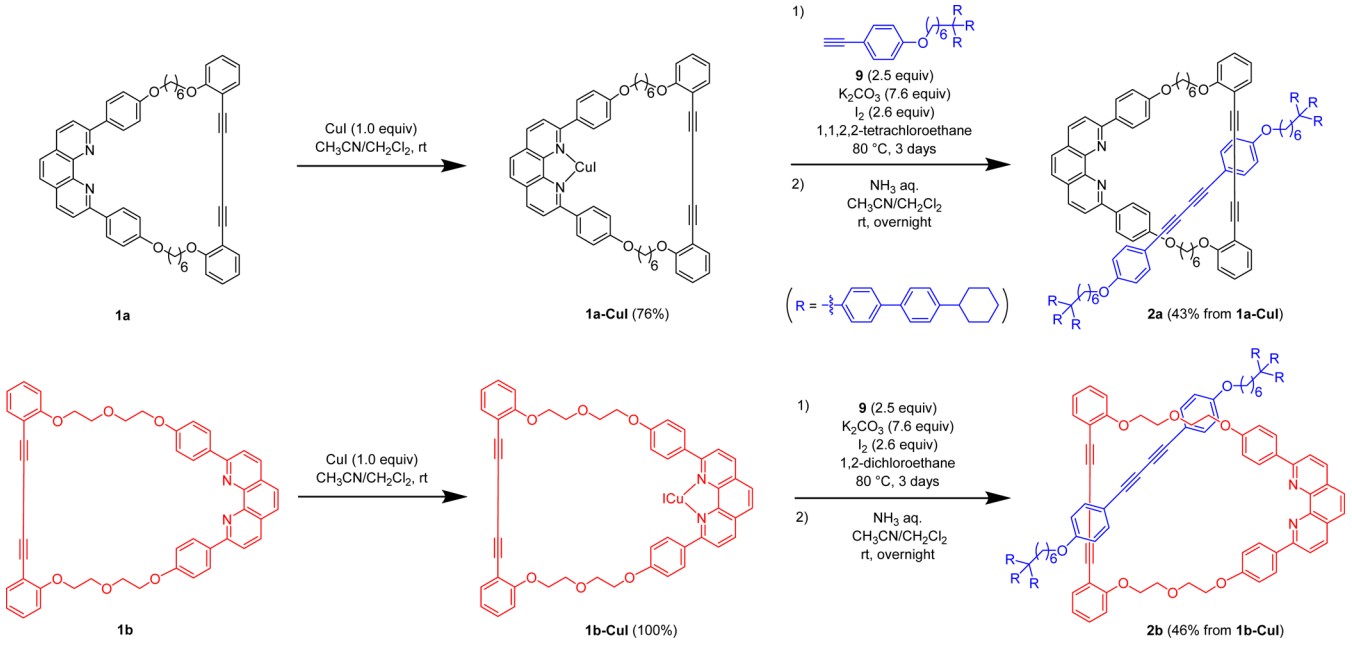
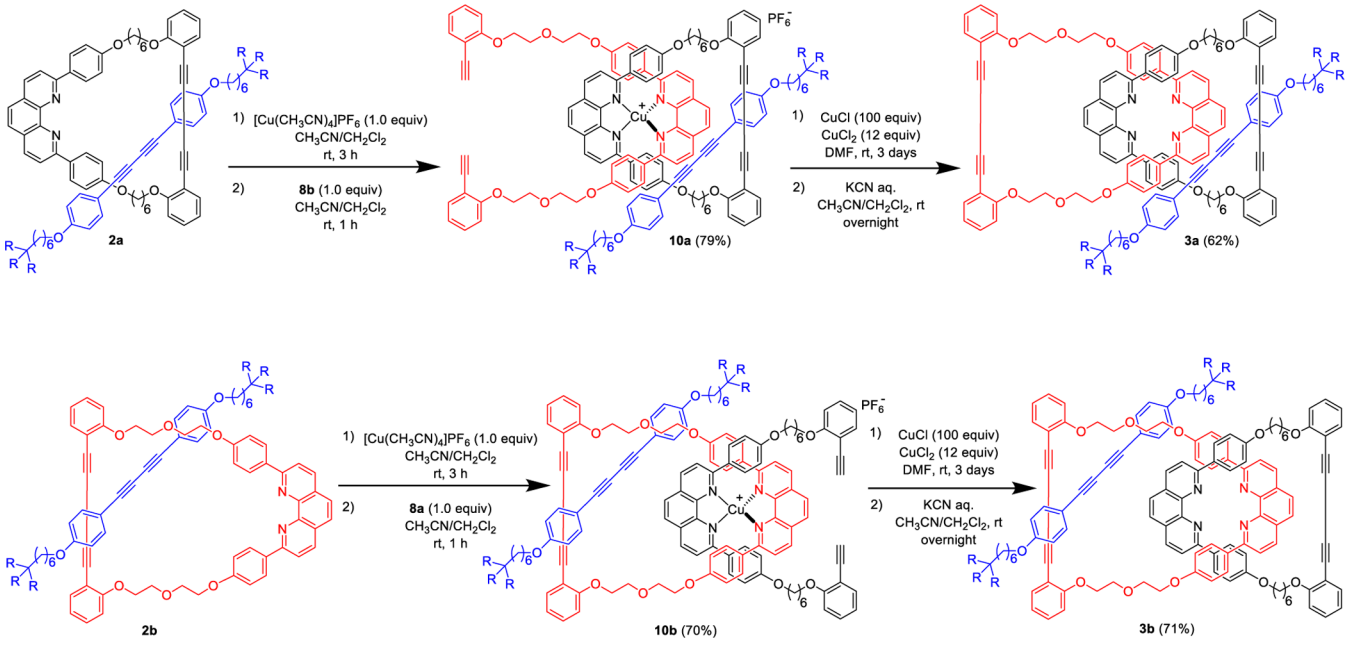
Scheme 3. Synthesis of [2]Rotaxanes by the Oxidative Coupling of Alkyne



Scheme 4. Synthesis of Rotacatenane Isomers



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 the 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 ^{1}H NMR spectra of [2]rotaxane **2a**, the macrocyclic phenanthroline **1a**, and the unthreaded axle component **11**[10h] are shown in Figure 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** ($H_{A\text{-}C}$) and the arylalkyne moieties of **11** (H_α) shifted upfield in **2a**. These upfield shifts were observed in many [2]rotaxanes we synthesized.[3e,5c,10h,i,11] On the other hand, the signal related to the protons of the *p*-alkoxyphenyl moieties (H_D) of **1a** shifted downfield in **2a**.

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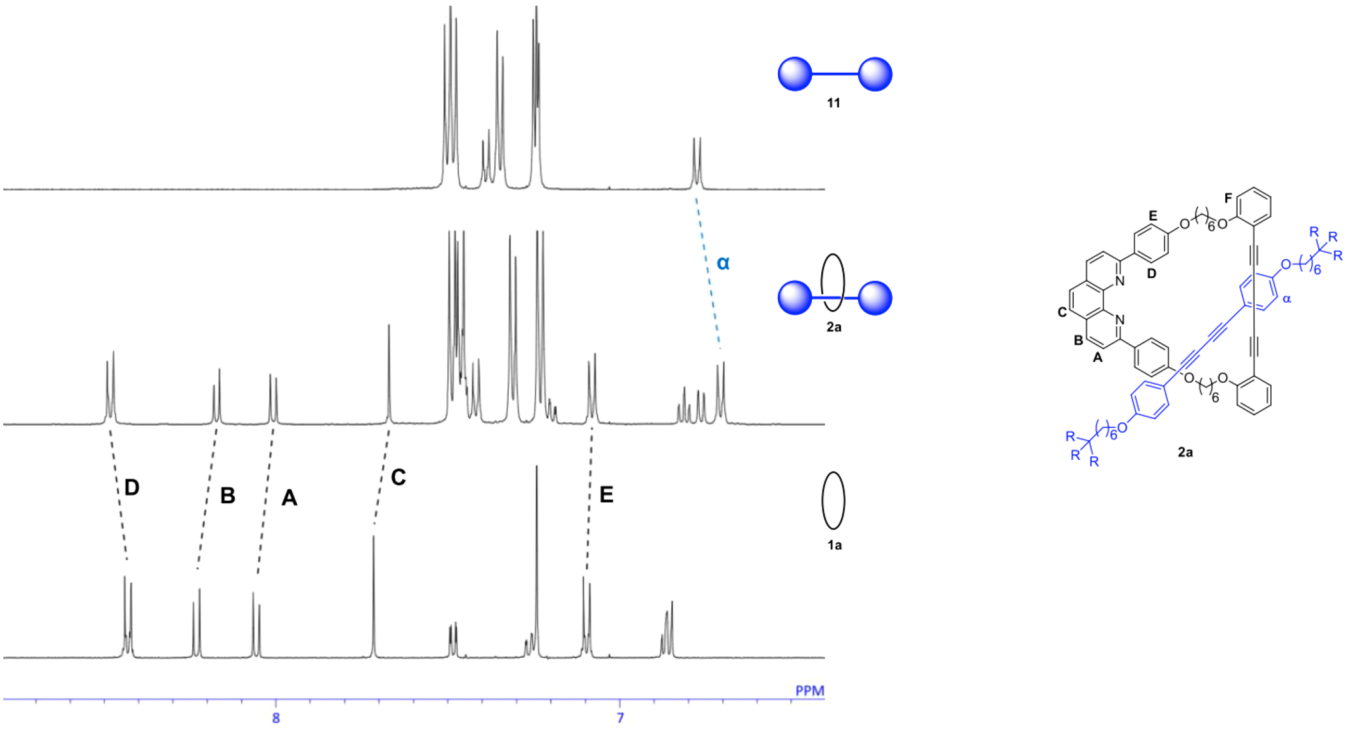

Figure 2. Partial ^{1}H NMR spectra of [2]rotaxane **2a** and related compounds (500 MHz, $CDCl_3$).

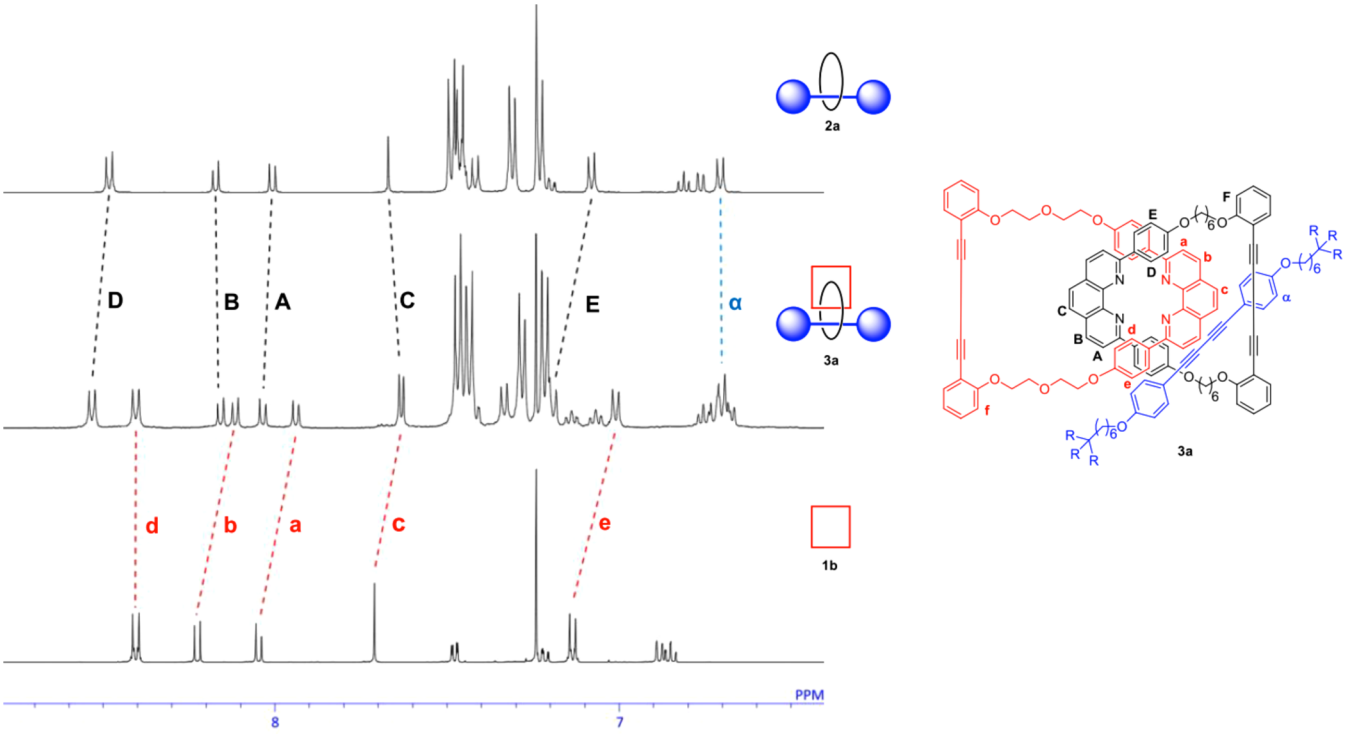

Figure 3. Partial ^{1}H NMR spectra of rotacatenane **3a** and related compounds (500 MHz, $CDCl_3$).

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.[20] The signals of some protons of **2a** and those of many protons of **1b** were shifted upfield in **3a**. For example, the signals of $H_{B,C,\alpha}$ of **2a** shifted upfield in **3a**. Additionally, the signals of the protons of the phenanthroline moiety ($H_{a\text{-}c}$) 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). 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**.[21]

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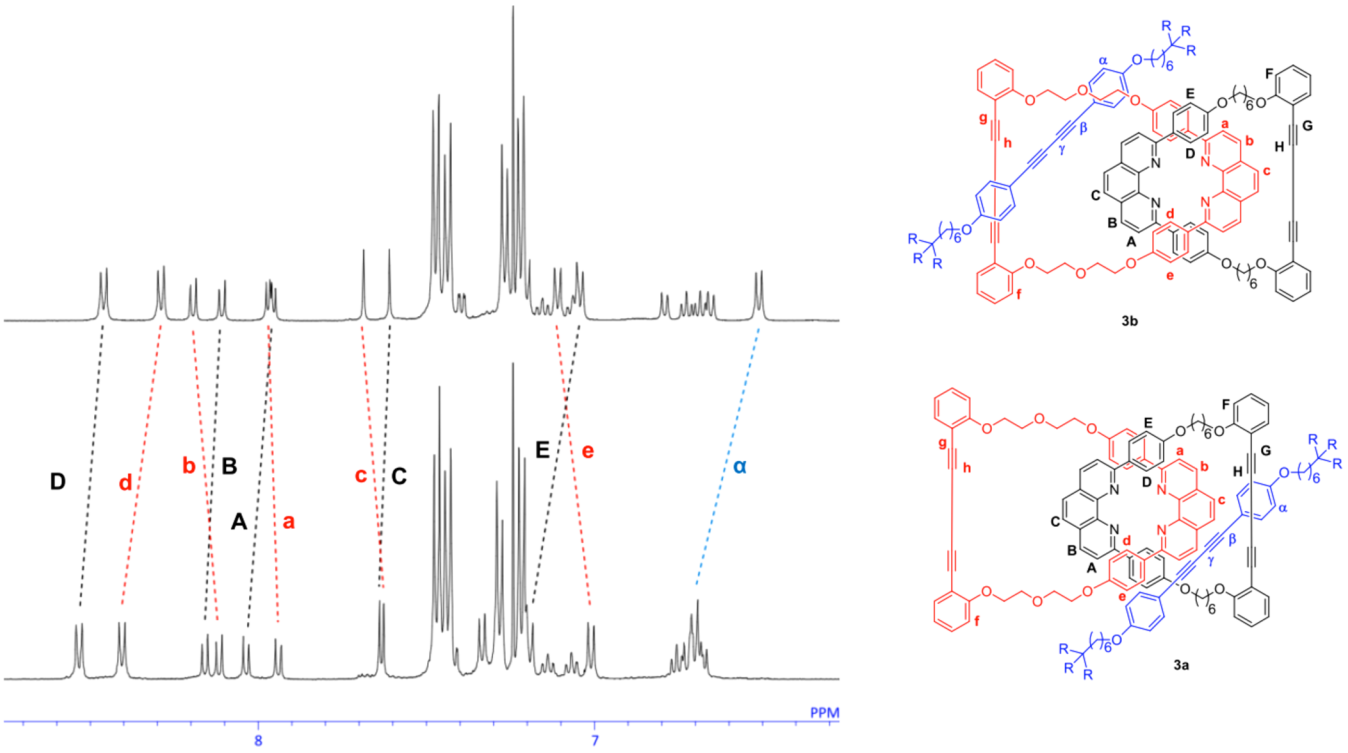

Figure 4. Partial ^{1}H NMR spectra of **3a,b** (500 MHz, $CDCl_3$).

We compared the NMR spectra of the rotacatenane isomers and found that the spectra of the isomers (**3a,b**) were significantly different (Figure 4). Some proton signals 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**, and the orders of the signals of H_A and H_a were different in **3a,b**. The same results were observed in the signals 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 proton signal of the axle component significantly shifted upfield when the axle component was passing through the smaller ring component (**1b**). The signal of H_α, which overlapped with other signals, appeared at 6.7 ppm in **3a** and appeared at 6.51 ppm in **3b**. We observed a similar difference in the chemical shifts in the NMR spectra of [3]rotaxanes (type 2.1).[3f]

Compared to the ^{1}H NMR spectra, the ^{13}C NMR spectra were generally less influenced by the difference of the connectivity in the interlocked compounds. Interestingly, we found that the difference in connectivity influenced the ^{13}C chemical shifts of **3a,b** 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 that appeared at 70−82 ppm (Figure 5).[22] 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**. The signal appeared at 79.4 ppm in **3b**. The carbon signals of the alkoxyphenyl moieties of the axle component ($C_{\beta,\gamma}$) shifted downfield when the axle component was passing through a smaller ring component (**1b**). The signal of C_β was observed at

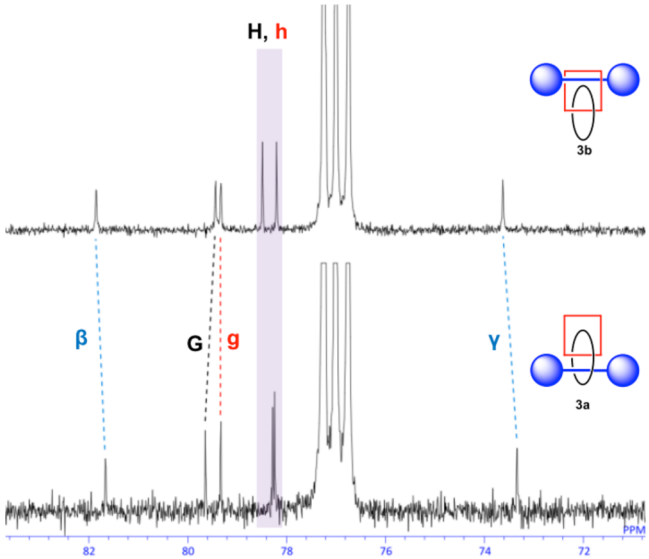

Figure 5. Partial ^{13}C NMR spectra of **3a,b** (126 MHz, $CDCl_3$). For the assignment of the signals, see Figure 4.

81.7 ppm in **3a**, whereas this signal appeared at 81.9 ppm in **3b**. The signal of C_γ, which appeared at 73.3 ppm in **3a**, also shifted downfield in **3b** (73.6 ppm).

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

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rotacatenane isomers were distinguished by ^{1}H and ^{13}C NMR spectroscopy. The study will contribute to the understanding of the chemistry of complex interlocked compounds.

EXPERIMENTAL SECTION

Compounds **4**,[14a] **7**,[11a,12c,15] **5b**,[23] **9**,[11b] and **11**[10h] were prepared according to the reported procedures. Compound **5a** and other reagents were commercially available and used without further purification. NMR 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) or 1,1,2,2-tetrachloroethane-d_2 (6.0 ppm for ^{1}H NMR and 73.8 ppm for ^{13}C NMR). Multiplicity is indicated by s (singlet), d (doublet), t (triplet), or m (multiplet). Coupling constants, *J*, are reported in Hz. A recycling preparative HPLC, equipped with a 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). High-resolution mass spectra (HR-MS) were obtained by using a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (ESI) or a time-of-flight mass analyzer (MALDI-TOF).

((2-((6-Chlorohexyl)oxy)phenyl)ethynyl)trimethylsilane (6a). A reported procedure[14b] 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 overnight, the solvent was removed *in vacuo*. The crude product was purified by silica gel column chromatography using hexane and CH_2Cl_2 (8:1 (v/v)) to afford **6a** (1.9 g, 6.1 mmol) in a 90% yield as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.

((2-(2-(2-Bromoethoxy)ethoxy)phenyl)ethynyl)trimethylsilane (6b). A reported procedure[14b] was generally followed to synthesize **6b**. To a solution of **4** (2.5 g, 13 mmol) and PPh_3 (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 overnight, the solvent was removed *in vacuo*. The crude product was purified by silica gel column chromatography using hexane and CH_2Cl_2 (2:1 (v/v)) to afford **6b** (3.8 g, 11 mmol) in 86% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) 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); ^{13}C NMR (76 MHz, $CDCl_3$) 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 $C_{15}H_{21}BrO_2Si$: C, 52.78; H, 6.20. Found: C, 52.81; H, 6.18.

2,9-Bis(4-((6-(2-ethynylphenoxy)hexyl)oxy)phenyl)-1,10-phenanthroline (8a). A reported procedure[5c] 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 K_2CO_3 (4.3 g, 31 mmol) in DMSO (23 mL) was stirred at 70 °C for 5 h. The solvent was removed *in vacuo*, and CH_2Cl_2 and H_2O were added to the residue. The organic and aqueous layers were each separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated. The crude product was purified by silica gel column chromatography using hexane and CH_2Cl_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}H NMR (500 MHz, $CDCl_3$) δ 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), 1.67−1.54 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 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; 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 $C_{52}H_{49}N_2O_4$ ([M + H]$^+$): 765.36868. Found: 765.36855.

2,9-Bis(4-(2-(2-(2-ethynylphenoxy)ethoxy)ethoxy)phenyl)-1,10-phenanthroline (8b). A reported procedure[5c] 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 K_2CO_3 (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 CH_2Cl_2 and H_2O were added to the residue. The organic and aqueous layers were each separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated. The crude product was purified by silica gel column chromatography using hexane and CH_2Cl_2 (1:4 (v/v)) to afford **8b** (0.47 g, 0.64 mmol) in 89% yield as a yellow amorphous solid; ^{1}H NMR (300 MHz, $CDCl_3$) 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, 4H), 4.32−4.19 (m, 8H), 4.10−3.95 (m, 8H), 3.24 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{48}H_{41}N_2O_6$ ([M + H]$^+$): 741.29591: Found: 741.29615.

Macrocyclic Phenanthroline (1a). To a mixture of **8a** (0.16 g, 0.21 mmol), CuCl (2.1 g, 21 mmol), and $CuCl_2$ (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 *in vacuo*. CH_2Cl_2 and 2 M HCl were added to the residue, and the organic and aqueous layers were each separated. After the extraction of the aqueous layer with CH_2Cl_2, the combined organic layer was washed with water and dried over Na_2SO_4. After the solvent was removed *in vacuo*, the residue was dissolved in CH_2Cl_2 (6 mL) and CH_3CN (28 mL). To the solution was added NH_3 aq. (30% solution, 24 mL), and the mixture was stirred at room temperature 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 separatory funnel, and the aqueous and organic layers were each separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water and dried over Na_2SO_4. After the solvent was removed *in vacuo*, the residue was combined with the solid A and purified by silica gel column chromatography using $CHCl_3$ to afford **1a** (0.087 g, 0.11 mmol) in 55% yield as a pale yellow solid; mp 247.6−248.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $C_2D_2Cl_4$) 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 $C_{52}H_{47}N_2O_4$ ([M + H]$^+$): 763.35303. Found: 763.35159.

Macrocyclic Phenanthroline (1b). To a mixture of **8b** (0.2 g, 0.27 mmol), CuCl (2.7 g, 27 mmol), and $CuCl_2$ (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*. CH_2Cl_2 and 2 M HCl were added to the residue, and the organic and aqueous layers were each separated. After the extraction of the aqueous layer with CH_2Cl_2, the combined organic layer was washed with water and dried over Na_2SO_4. After the solvent was removed *in vacuo*, the residue

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was dissolved in CH_2Cl_2 (20 mL) and CH_3CN (47 mL). To the solution was added NH_3 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 and aqueous layers were each separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water and dried over Na_2SO_4. After the solvent was removed *in vacuo*, the residue was purified by silica gel column chromatography using $CHCl_3$ to afford **1b** (0.14 g, 0.19 mmol) in 71% yield as a pale yellow amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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, 1113, 1054, 923, 838, 796, 746, 513 cm^{-1}; HR-MS (ESI) Calcd for $C_{48}H_{39}N_2O_6$ ([M + H]$^+$): 739.28026. Found: 739.28032.

1a-CuI. A reported procedure[11a] was generally followed to synthesize **1a-CuI**. To a suspension of **1a** (0.22 g, 0.29 mmol) in CH_2Cl_2 (29 mL) and CH_3CN (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 $(CH_2Cl)_2$ 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; ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (151 MHz, $C_2D_2Cl_4$) 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 $C_{52}H_{46}N_2O_4{}^{63}Cu$ ([M − I]$^+$): 825.27481. Found: 825.27617.

1b-CuI. To a solution of **1b** (0.11 g, 0.15 mmol) in CH_2Cl_2 (7.5 mL) and CH_3CN (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 chromatography column using CH_2Cl_2 to afford **1b-CuI** (0.14 g, 0.15 mmol) in quantitative yield as a red amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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 $C_{48}H_{38}N_2O_6{}^{63}Cu$ ([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_2CO_3 (11 mg, 0.076 mmol), and I_2 (6.6 mg, 0.026 mmol) in dry $(CHCl_2)_2$ (1.0 mL) was stirred at 80 °C for 2 days, and K_2CO_3 (11 mg, 0.076 mmol) and I_2 (6.6 mg, 0.026 mmol) were added to the solution. After the mixture was stirred at 80 °C overnight, the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (2.5 mL) and CH_3CN (3.5 mL), and NH_3 aq. (30% solution, 1.7 mL) was added to the solution. After the mixture was stirred at room temperature overnight, CH_2Cl_2 and H_2O were added to the mixture. The organic and aqueous layers were each separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water and dried over Na_2SO_4. After the solvent was removed *in vacuo*, the residue was purified by silica gel column chromatography using hexane and CH_2Cl_2 (1:1 (v/v)) and GPC using $CHCl_3$ to afford **2a** (23 mg, 8.7 μmol) in 43% yield as a pale yellow amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 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); ^{13}C NMR (126 MHz, $CDCl_3$) δ 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, 30.1, 29.1, 29.0, 28.8, 26.9, 26.1, 25.8, 25.7, 25.5, 25.2; IR (ATR) 3026, 2921, 2850, 1602, 1489, 1281, 1243, 1169, 1004, 832, 810, 746, 524 cm^{-1}; HR-MS (ESI) Calcd for $C_{190}H_{193}N_2O_6$ ([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), K_2CO_3 (11 mg, 0.076 mmol), and I_2 (6.6 mg, 0.026 mmol) in $(CH_2Cl)_2$ (1.0 mL) was stirred at 80 °C for 2 days, and K_2CO_3 (11 mg, 0.076 mmol) and I_2 (6.6 mg, 0.026 mmol) were added to the mixture. After the mixture was stirred at 80 °C overnight, the residue was dissolved in CH_2Cl_2 (1.5 mL) and CH_3CN (3.5 mL), and NH_3 aq., (30% solution, 1.7 mL) was added to the solution. After the mixture was stirred at room temperature overnight, CH_2Cl_2 and H_2O were added to the resulting solution. The organic and aqueous layers were each separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water and dried over Na_2SO_4. After the solvent was removed *in vacuo*, the residue was purified by silica gel column chromatography using hexane and CH_2Cl_2 (1:2 (v/v)) and GPC using $CHCl_3$ to afford **2b** (24 mg, 9.2 μmol) in 46% yield as a yellow amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 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 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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, 1004, 832, 779, 529 cm^{-1}; HR-MS (ESI) Calcd for $C_{186}H_{185}N_2O_8$ ([M + H]$^+$): 2574.41254. Found: 2574.40830.

Tetrahedral Cu(I) Complex (10a). A reported procedure[5c] was generally followed to synthesize **10a**. To a solution of $[Cu(CH_3CN)_4]PF_6$ (8.8 mg, 0.024 mmol) in dry CH_3CN (3.4 mL) was added a solution of **2a** (61 mg, 0.024 mmol) in CH_2Cl_2 (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 CH_2Cl_2 (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 CH_2Cl_2 to afford **10a** (67 mg, 0.019 mmol) in 79% yield as a brown amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) 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), 7.33 (d, J = 8.5 Hz, 12H), 7.31−7.21 (m, 20H), 7.19 (d, J = 8.5 Hz, 4H), 7.07 (d, J = 8.5 Hz, 4H), 6.93 (d, J = 9.0 Hz, 2H), 6.91−6.84 (m, 4H), 6.82 (d, J = 8.5 Hz, 2H), 6.59 (d, J = 8.5 Hz, 4H), 6.04 (d, J = 8.5 Hz, 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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,

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J. Org. Chem. 2016, 81, 1175−1184

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, 111.7, 111.3, 81.4, 80.2, 79.4, 78.2, 73.2, 69.8, 69.7, 68.7, 68.5, 68.0, 67.5, 67.4, 55.9, 44.1, 40.4, 34.4, 30.2, 29.3, 29.2, 29.1, 26.8, 26.6, 26.1, 25.8, 25.3; IR (ATR) 3281, 3027, 2922, 2850, 1602, 1489, 1472, 1445, 1281, 1246, 1170, 1134, 1110, 1048, 1004, 832, 812, 779, 748, 667, 556, 540, 531, 511 cm^{-1}; HR-MS (MALDI-TOF) Calcd for $C_{238}H_{232}N_4O_{12}Cu$ ($[M - PF_6]^+$): 3400.6957. Found: 3400.6845.

Tetrahedral Cu(I) Complex (10b). A reported procedure[5c] was generally followed to synthesize **10b**. To a solution of $[Cu(CH_3CN)_4]PF_6$ (10 mg, 0.027 mmol) in CH_3CN (4.0 mL) was added a solution of **2b** (70 mg, 0.027 mmol) in CH_2Cl_2 (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 CH_2Cl_2 (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 CH_2Cl_2 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, $CDCl_3$) 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), 1.57−1.49 (m, 4H), 1.49−1.04 (m, 50H); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $CuCl_2$ (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*, CH_2Cl_2 and H_2O were added to the residue. The organic and aqueous layers were each separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated. The residue was passed through a short silica gel chromatography column using CH_2Cl_2 and MeOH (10:1 (v/v)), and evaporation of the solvent gave the amorphous solid. The amorphous solid was dissolved in CH_2Cl_2 (3.8 mL), CH_3CN (3.8 mL), and H_2O (3.8 mL), and KCN (0.58 g) was added to the solution. After the mixture was stirred at room temperature overnight, CH_2Cl_2 and H_2O were added to the resulting solution. The organic and aqueous layers were each separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography using CH_2Cl_2 and AcOEt (15:1 (v/v)) and GPC using $CHCl_3$ to afford **3a** (39 mg, 0.012 mmol) in 62% yield as a yellow amorphous solid; ^1H NMR (500 MHz, $CDCl_3$) 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), 7.28 (d, J = 8.0 Hz, 12H), 7.25−7.17 (m, 16H), 7.14 (t, J = 7.3 Hz, 2H), 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{238}H_{231}N_4O_{12}$ ($[M + H]^+$): 3336.7583. Found: 3336.7358.

Rotacatenane (3b). A mixture of **10b** (67 mg, 0.019 mmol), CuCl (0.19 g, 1.9 mmol), and $CuCl_2$ (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*, CH_2Cl_2 and H_2O were added to the residue. The organic and aqueous layers were each separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated. The residue was passed through a short silica gel chromatography column using CH_2Cl_2 and MeOH (10:1 (v/v)), and evaporation of the solvent gave the amorphous solid. The amorphous solid was dissolved in CH_2Cl_2 (3.8 mL), CH_3CN (3.8 mL), and H_2O (3.8 mL), and KCN (0.58 g) was added to the solution. After the solution was stirred at room temperature overnight, CH_2Cl_2 and H_2O were added to the resulting solution. The organic and aqueous layers were each separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography using CH_2Cl_2 and AcOEt (20:1 (v/v)) and GPC using $CHCl_3$ to afford **3b** (45 mg, 0.013 mmol) in 71% yield as a yellow amorphous solid; ^1H NMR (500 MHz, $CDCl_3$) 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, 14H), 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{238}H_{231}N_4O_{12}$ ($[M + H]^+$): 3336.7583. Found: 3336.7535.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02697.

NMR spectra (^1H, ^{13}C, COSY, HMBC, NOESY) for new compounds; the comparison of ^1H NMR spectra of **2b**, **3b**, and related compounds, and MALDI-TOF MS spectra (observed and simulated) of **10a,b** and **3a** (PDF)

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Notes

The authors declare no competing financial interest.

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J. Org. Chem. 2016, 81, 1175−1184

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(21) See Supporting Information.

(22) The assignments of these signals were based on the HMBC spectra of **3a,b**.

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