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Synthesis of Large [2]Rotaxanes. The Relationship between the Size of the Blocking Group and the Stability of the Rotaxane

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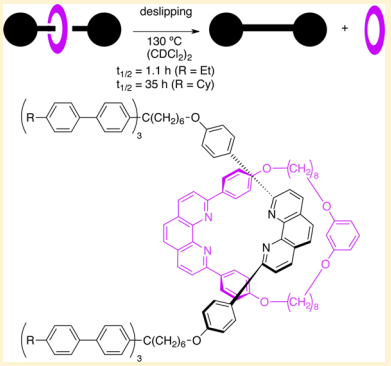
Supporting Information

ABSTRACT: [2]Rotaxanes with large macrocyclic phenanthrolines were prepared by the template method, and the stability of the rotaxanes was examined. Compared to the tris(biphenyl)methyl group, the tris(4-cyclohexylbiphenyl)methyl group was a larger blocking group, and the rate of the dissociation of the components decreased significantly when the thermal stability of a rotaxane with a 41-memebered ring was examined. We also succeeded in the synthesis of larger rotaxanes by the oxidative dimerization of alkynes with these bulky blocking groups, utilizing the catalytic activity of the macrocyclic phenanthroline−Cu complex.



INTRODUCTION

Interlocked compounds such as rotaxanes and catenanes are synthetically challenging molecules, and various synthetic methods have been reported to date.[1] The template method is an efficient approach for the synthesis of interlocked compounds, and this method has been applied for the synthesis of various interlocked structures.[2] In many examples, the products were isolated in good to high yields, making this method very attractive for the synthesis of complex interlocked compounds.

A [2]rotaxane consists of a dumbbell-shaped component and a ring component. The dissociation of the two components is suppressed when high activation energy is required for the dissociation (deslipping) of the components. Therefore, a bulky "dumbbell" is required for the synthesis of a stable rotaxane[3] when no attractive interaction exists between the components. The relationship between the size of the components and the stability of the rotaxanes has been studied by several groups.[4] For example, the spatial demand of dendrimers has been examined by observing the stability of the rotaxanes with blocking groups derived from dendrimers.[4i] We recently reported the synthesis of rotaxanes which consisted of a large ring component (macrocyclic phenanthroline) and a large blocking group (tris(biphenyl)methyl group) by the template method and examined the stability of the rotaxanes (Figure 1).[4m] While a rotaxane with a 33-membered phenanthroline ring (**1a**) was stable at 60 °C in $CDCl_3$, the dissociation of the components was observed when a rotaxane with 37-membered ring (**1b**) was heated to 60 °C. The attempted isolation of a rotaxane with a larger ring (**1c**, a 41-membered ring) failed. These results prompted us to design and study the stability of rotaxanes with larger blocking groups. In this study, we report the synthesis and the stability of large [2]rotaxanes.

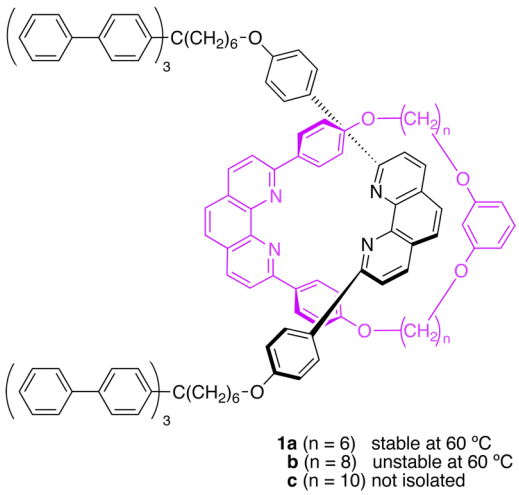


Figure 1. Stability of [2]rotaxanes (**1a−c**) with various ring sizes (ref 4m).

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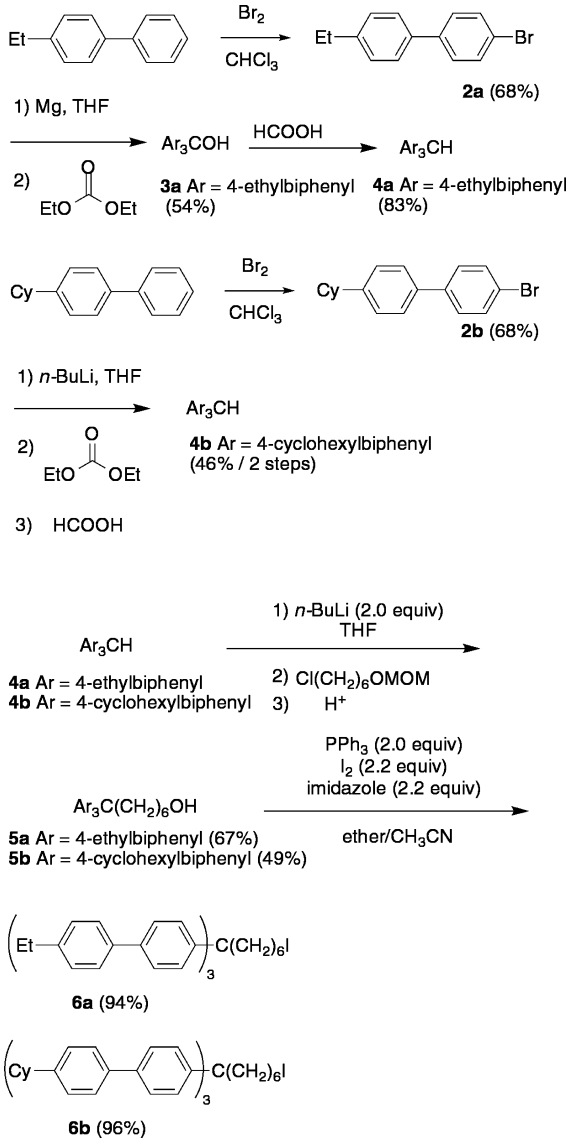
RESULTS AND DISCUSSION

Synthesis of Large [2]Rotaxanes. The introduction of a substituent to the biphenyl group is a simple and efficient method for the synthesis of a larger blocking group than tris(biphenyl)methyl group. We designed and synthesized alkyl iodides with the tris(4-ethylbiphenyl)methyl group and tris(4-cyclohexylbiphenyl)methyl group as the precursors for the dumbbell-shaped moiety of the rotaxanes. The procedures we previously developed[4m] for similar compounds were applied for the synthesis of these compounds (Scheme 1).

Scheme 1



Triarylmethanes were synthesized from 4-substituted biphenyls. Thus, 4-ethylbiphenyl was brominated, and the product was treated with Mg and ethyl carbonate to give tris(4-ethylbiphenyl)methanol (**3a**) in good yield. The alcohol was reduced by formic acid to yield tris(4-ethylbiphenyl)-methane (**4a**) in 83% yield. Tris(4-cyclohexylbiphenyl)methane (**4b**) was prepared from 4-cyclohexylbiphenyl. The reaction of the Grignard reagent prepared from **2b** with ethyl carbonate did not proceed efficiently, and the yield of the product was low. The triarylmethanol was prepared in a better yield by the treatment of the aryllithium, which was prepared by the treatment of **2b** with *n*-BuLi and ethyl carbonate, and the crude product was used for the next reaction without purification. Tris(4-cyclohexylbiphenyl)methane (**4b**) was synthesized in 46% yield from **2b**. Alcohols with large blocking groups (**5a**,**b**) were synthesized by the reaction of lithiated triarylmethanes with 1-chloro-6-(methoxymethoxy)hexane and the removal of the methoxymethyl group. The alcohols were converted to the iodides (**6a**,**b**) by PPh_3-I_2-imidazole in high yields.

[2]Rotaxanes with large rings and dumbbells were prepared by template method.[4m,5] Thus, the tetrahedral Cu complexes were prepared in situ from **7**,[4m] **8**,[5] and $[Cu(CH_3CN)_4]PF_6$. The complexes reacted with iodide **6**, and the copper ion was removed from the phenanthroline ligand by the treatment of the crude product with an excess of KCN. The results were summarized in Table 1.

The rotaxane was synthesized in good yield when **7a**, **8**, and **6a** were used as the substrates (entry 1). These results are in accordance with our previous results,[4m] where the tris-(biphenyl)methyl group, which is a smaller group, turned out to be a suitable blocking group for the synthesis of a stable rotaxane composed of **7a**. Even with a larger phenanthroline derivative (**7b**), the corresponding rotaxane was isolated in 64% yield (entry 2): the dissociation of the rotaxanes was not observed during the purification of the products.[6] The result indicated the increased stability[7] of the rotaxane by using a larger blocking group, tris(4-ethylbiphenyl)methyl group, since a rotaxane composed of **7b** and an axle with a smaller blocking group (tris(biphenyl)methyl group) turned out to be labile, and the dissociation of the components (deslipping reaction) was observed at 60 °C.[4m] Though we expected that a stable rotaxane would be isolated when this large blocking group was used to synthesize rotaxanes with a 41-memebered macrocycle (**7c**), the corresponding rotaxane was not detected, and instead, we isolated the coupling product (**11a**) and **7c** in high yields (entry 3).

Expecting a higher stability of the corresponding rotaxanes, we carried out the synthesis of rotaxanes with a very large blocking group, tris(4-cyclohexylbiphenyl)methyl group, by the reaction of **7a**−**c**, **8**, and **6b**. As expected, the corresponding rotaxanes were prepared in good yields when smaller macrocyclic phenanthroline complexes such as **7a** or **7b** were used as the starting materials (entries 4 and 5). Disappointingly, the attempted synthesis of a larger rotaxane, which was composed of **7c**, failed (entry 6). The result indicated that the size of the ring of **7c** was too large, and even a very bulky blocking group (tris(4-cyclohexylbiphenyl)methyl group) could pass through the ring with very low energy barrier.[8]

Thermal Stability of Large [2]Rotaxanes. Since we isolated some larger rotaxanes that did not dissociate during standard purification, we were interested in the thermal stability of these compounds at elevated temperature. Solutions of rotaxanes in 1,1,2,2-tetrachloroethane-d_2 were heated to 70−140 °C. The deslipping reaction was monitored by NMR.[5] The kinetic paremeters were determined, and the results are summarized in Table 2.

We have already reported[4m] that the dissociation of the components (deslipping reaction) was observed at 60 °C for **1b**, and the estimated half-life of the rotaxane at 130 °C was less than 0.5 h (entry 1). We expected that the rotaxanes (**10a**,**b**,**d**,**e**) would be stable because a bulkier blocking group was introduced and the deslipping reaction would not proceed easily. The progress of the deslipping reaction, however, was

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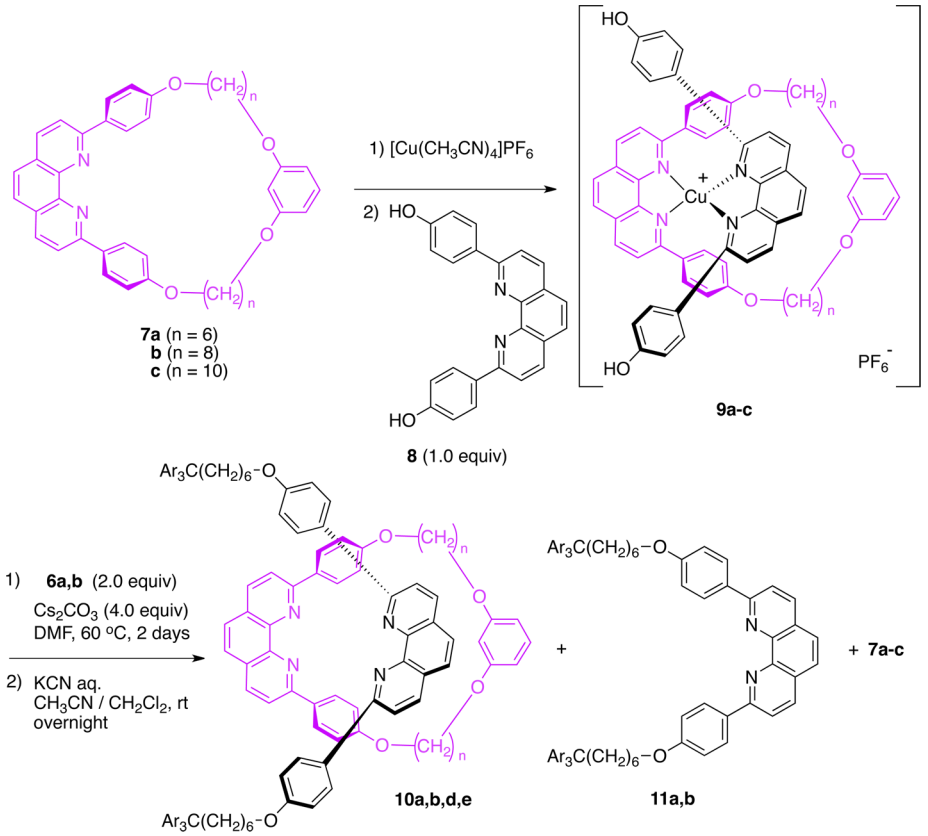
Table 1. Template Synthesis of [2]Rotaxanes with Various Blocking Groups and Rings



entry	7	6	rotaxane 10	yield (%)	11	yield (%)	recovery of 7 (%)
1	7a	6a (R=Et)	10a	60	11a	21	38
2	7b	6a	10b	64	11a	17	28
3	7c	6a	10c	0	11a	78	91
4	7a	6b (R=Cy)	10d	51	11b	18	36
5	7b	6b	10e	54	11b	19	31
6	7c	6b	10f	0	11b	63	88

observed at elevated temperature. For example, very slow dissociation of **10a**, which is composed of a larger blocking group (tris(4-ethylbiphenyl)methyl group), was observed at 130 °C, and 20% of **10a** dissociated after heating a solution of **10a** for 10 days (entry 2). The progress of the deslipping reaction was faster when the rotaxane was composed of a larger ring (**1b**) and the estimated half-life of **10b** at 130 °C was 1.1 h (entry 3). Compound **10d** turned out to be very stable, and the dissociation did not proceeded when a solution of **10d** was heated at 130 °C for 10 days (entry 4). Though a rotaxane with a larger blocking group (**10e**) was more stable compared to **10b**, the dissociation slowly proceeded at 130 °C (entry 5). It is noteworthy that even a rotaxane with a very bulky blocking group (tris(4-cyclohexylbiphenyl)methyl group) still dissociated when a 37-membered ring (**1b**) was used as the ring component of the rotaxane. The observed high entropic contribution in these reactions is in accordance with our previous results.[4m] Though it is difficult to explain the difference of the kinetic parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) observed in these reactions, it has already been reported that these parameters are strongly affected by changing the structure of the rotaxane.[4j]

Synthesis of Large [2]Rotaxanes using the Oxidative Dimerization Reaction Mediated by Macrocyclic Phenanthroline–Cu Complexes. Based on the results of the deslipping reactions, we expected that rotaxanes composed of **7a,b** as the ring component and tris(4-cyclohexylbiphenyl)-methyl group as the blocking group would be synthesized as stable compounds. Leigh et al.[10] and our group[11] recently developed a conceptually new and efficient method for the synthesis of rotaxanes and catenanes.[12] The catalytic activity of the macrocyclic metal complex was utilized for the coupling reactions of substrates with bulky substituents, and the rotaxanes were isolated in good to high yields. For example, the oxidative dimerization reaction of alkynes was mediated by macrocyclic phenanthroline–Cu complexes, providing an efficient method for the synthesis of [2]rotaxanes.[11a] We applied this methodology for the synthesis of larger [2]-rotaxanes with new dumbbell moieties. We prepared an arylalkyne (**13**) with tris(4-cyclohexylbiphenyl)methyl group as the blocking group by the reaction of **6a** and **12** (Scheme 2). The reactions of **13** with macrocyclic phenanthroline–Cu complexes (**14a,b**)[11] were carried out in the presence of I_2 as the oxidant and K_2CO_3 as the base (Scheme 3). The rotaxane (**15a**) was isolated in 82% yield when a smaller macrocyclic phenanthroline–Cu complex (**14a**) was reacted with a small excess of **13**. We also succeeded in the synthesis of the rotaxane (**15b**) when we carried out the reaction of **13** with a larger

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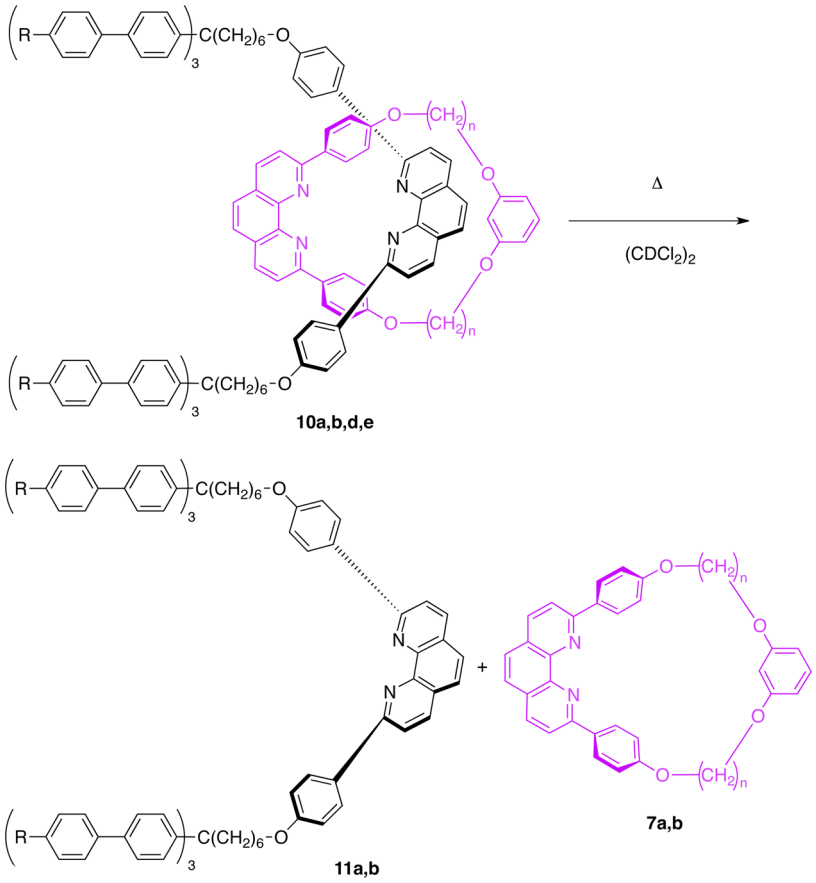
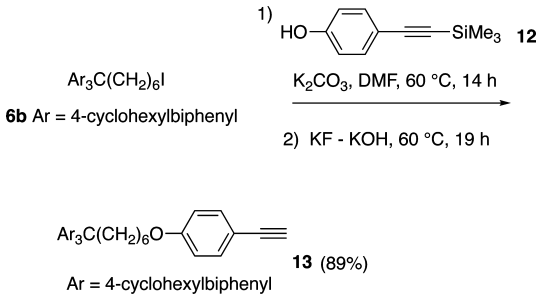
Table 2. Dissociation of [2]Rotaxanes



entry	cmpd	R	n	$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta S^{\ddagger}$ (J/(mol·K))	$\Delta G^{\ddagger}$ (403 K) (kJ/mol)	$t_{1/2}$ (403 K) (h)[a]
1[b]	**1b**	H	6	65.0	−144	123	<0.5
2	**10a**	Et	6				*c*
3	**10b**	Et	8	80.9	−119	129	1.1
4	**10d**	Cy	6				*d*
5	**10e**	Cy	8	64.8	−212	150	35

[a]Estimated by kinetic parameters. [b]Values from ref 4m. This reaction was carried out in $CDCl_3$. [c]Ca. 20% of the substrate dissociated after heating for 10 days (240 h). [d]The dissociation of the substrate was not observed after heating for 10 days (240 h).

Scheme 2



copper complex (**14b**). As expected, the rotaxanes (**15a,b**) were stable and the deslipping reaction did not proceed when the compounds were treated at rt or at elevated temperature (40 °C). The observed lower yield of **15b** might be due to the progress of the deslipping reaction[13] during the synthesis of **15b**, since the reaction was carried out at 130 °C. Alternatively, the efficiency of the threading reaction might have decreased due to the increased flexibility of the macrocyclic ring. Thus, the macrocyclic compound might adopt bent (folded) conformation, especially when the ring is large (and flexible), and the bond-forming reaction may not proceed inside the ring. In this case, the formation of the rotaxane would not be observed, and the coupling reaction would proceed without threading of the axle component.

■ CONCLUSION

We synthesized a series of rotaxanes by template method and studied the relationship between the size of the blocking group and the stability of the rotaxane. The structures of some rotaxanes with a large ring component (37-membered ring) were stabilized by introducing bulkier blocking groups such as tris(4-cyclohexylbiphenyl)methyl group. Further application of these large blocking groups to the synthesis of interlocked compounds is ongoing.

■ EXPERIMENTAL SECTION

Commercially available reagents were purchased and used without further purification unless otherwise noted. 4-Cyclohexylbiphenyl[14] was prepared by the cobalt-catalyzed reaction[15] of bromocyclohexane with the corresponding Grignard reagent ([1,1′-biphenyl]-4-ylmagnesium bromide). Macrocyclic phenanthrolines (**7a–c**)[4m] and macro-

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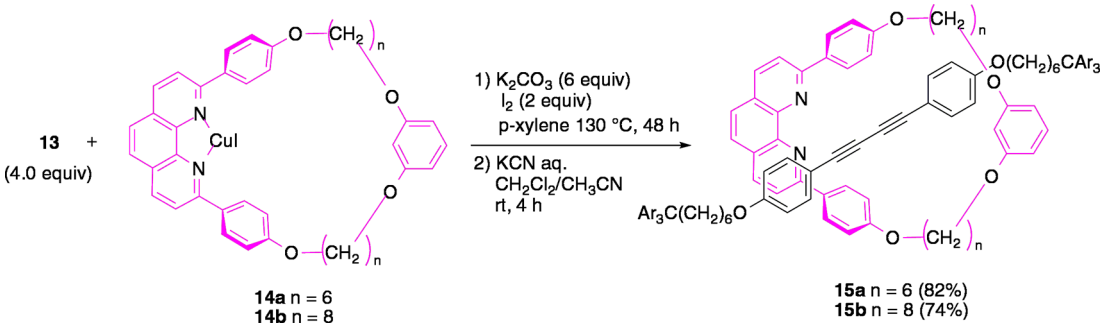
Scheme 3



cyclic phenanthroline–Cu complexes (**14a,b**)[11] were prepared as reported. Chemical shifts were reported in δ relative to chloroform (7.24 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR) or dimethyl sulfoxide (2.49 ppm for ^{1}H NMR and 39.7 ppm for ^{13}C NMR).

4-Ethylbiphenyl. To a stirred solution of 4-acetylbiphenyl[16] (45.3 g, 230 mmol) and 3 mL of concd H_2SO_4 in EtOH (240 mL) was added 5% Pd/C (4.53 g) under argon atmosphere. The mixture was stirred vigorously and heated at 60 °C for 2 days under hydrogen (1 atm). The mixture was filtered, and the solvent was evaporated to give colorless oil, which was purified by distillation (110 °C, 1.1 mmHg): yield 30.5 g (73%).

4-Bromo-4′-ethylbiphenyl (2a).[17] A solution of bromine (9.0 mL, 176 mmol) in chloroform (90 mL) was added to the mixture of 4-ethylbiphenyl (30.5 g, 167 mmol) in chloroform (140 mL) at rt. The mixture was stirred in the dark for 24 h at rt. The solution was poured into 2 M NaOH aq and stirred for 1 h. The mixture was diluted with dichloromethane, washed with water, dried over $MgSO_4$, and concentrated in vacuo. The resulting colorless solid was recrystallized from ethanol to afford **2a**: yield 29.8 g (68%).

Tris(4′-ethyl[1,1′-biphenyl]-4-yl)methanol (3a). In a three-necked flask equipped with a condenser, dropping funnel, and magnetic stirrer were placed magnesium turnings (0.76 g, 45 mmol) anhydrous THF (4 mL) under Ar. 4-Bromo-4′-ethylbiphenyl (**2a**, 7.86 g, 30 mmol) in anhydrous THF (18 mL) was added dropwise over 30 min (exothermic). The mixture was refluxed for 30 min. Methyl carbonate (0.76 mL, 9.0 mmol) was added slowly at 0 °C, and the mixture was refluxed for 1 h. The mixture was cooled to rt, neutralized with 10% HCl, and extracted with dichloromethane. The combined organic layer was washed with water and dried over $MgSO_4$. A yellow solid was obtained after removal of the solvent by evaporation. The solid was purified by silica gel column chromatography (Hex/CH_2Cl_2 = 3:1): yield 3.09 g (54%); mp 182–183 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, J = 8.4 Hz, 6 H), 7.51 (d, J = 8.4 Hz, 6 H), 7.40 (d, J = 8.4 Hz, 6 H), 7.25 (d, J = 8.4 Hz, 6 H), 2.83 (s, 1 H), 2.67 (q, J = 7.6 Hz, 6 H), 1.26 (t, J = 7.5 Hz, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) 145.5, δ 143.5, 140.1, 138.0, 128.3 (overlap), 127.0, 126.5, 81.7, 28.5, 15.6; IR (KBr) 3447, 3024, 2963, 2929, 2871, 1906, 1559, 1496, 1454, 1395, 1329, 1266, 1190, 1157, 1117, 1005, 911, 849, 819, 789, 698, 591, 522 cm^{-1}. Anal. Calcd for $C_{43}H_{40}O$: C, 90.17; H, 7.04. Found: C, 90.19; H, 7.01.

Tris(4′-ethyl[1,1′-biphenyl]-4-yl)methane (4a). A mixture of **3a** (1.36 g, 2.38 mmol), toluene (10 mL), and formic acid (5 mL) was refluxed for 12 h. The mixture was evaporated, and the residue was dissolved in CH_2Cl_2 (80 mL). The mixture was neutralized with K_2CO_3, dried over $MgSO_4$, and concentrated. The crude product was purified by recrystallization from Hex/$CHCl_3$ to afford **4a** as a colorless powder: yield 1.10 g (83%); mp 155–157 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, J = 7.6 Hz, 6 H), 7.50 (d, J = 7.6 Hz, 6 H), 7.24 (d, J = 7.8 Hz, 6 H), 7.23 (d, J = 7.8 Hz, 6 H), 5.62 (s, 1 H), 2.67 (q, J = 7.6 Hz, 6 H), 1.26 (t, J = 7.8 Hz, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ145.5, 143.3, 142.7, 139.2, 138.2, 129.8, 128.3, 126.9, 55.9, 28.5, 15.5; IR (KBr) 3447, 3022, 2962, 2928, 2869, 1908, 1792, 1700, 1653, 1607, 1577, 1559, 1496, 1452, 1398, 1374, 1310, 1271, 1193, 1117, 1059, 1030, 1005, 965, 868, 836 cm^{-1}. Anal. Calcd for $C_{43}H_{40}$: C, 92.76; H, 7.24. Found: C, 93.05; H, 7.29.

4-Bromo-4′-cyclohexylbiphenyl (2b). The procedure reported for the synthesis of **2a** was generally followed to synthesize **2b**. The crude product was purified by recrystallization from hexane to afford **2b** as colorless powder. Compound **2b** (28.0 g) was isolated in 78% yield from **1b** (27 g, 114 mmol). **2b**: mp 157–158 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 2.56–2.52 (m, 1H), 1.92–1.85 (m, 4H), 1.78–1.75 (m, 1H), 1.49–1.37 (m, 4H), 1.31–1.24 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7, 140.1, 137.4, 131.8, 128.6, 127.4, 126.8, 121.1, 44.2, 34.4, 26.9, 26.1; IR (KBr) 3060, 2921, 2849, 2665, 1902, 1606, 1481, 1447, 1388, 1138, 1121, 1076, 1000, 893, 811, 779, 743, 645, 553, 503 cm^{-1}. Anal. Calcd for $C_{18}H_{19}Br$: C, 68.58; H, 6.07. Found: C, 68.76; H, 6.14.

Tris(4′-cyclohexyl[1,1′-biphenyl]-4-yl)methanol (3b) and Tris(4′-cyclohexyl[1,1′-biphenyl]-4-yl)methane (4b). To a solution of **2b** (11.4 g, 36 mmol) in anhydrous THF (90 mL) was added n-BuLi (1.6 M in hexane, 23 mL, 36 mmol) dropwise over 30 min at −78 °C under Ar. The reaction mixture was stirred for 1 h. To the mixture was added dimethyl carbonate (1.0 mL, 12 mmol) at −78 °C. The resulting mixture was stirred overnight, while the temperature of the mixture was allowed to reach to rt. The solution was quenched with MeOH (50 mL), and the solvent was removed by evaporation to afford crude tris(4′-cyclohexyl[1,1′-biphenyl]-4-yl)methanol (11.2 g) as a yellow solid, which was employed for the next reaction without purification. This compound could be purified by recrystallization (CH_2Cl_2–hexane).

3b: mp 204–205 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 8.8 Hz, 6H), 7.51 (d, J = 8.4 Hz, 6H), 7.38 (d, J = 8.4 Hz, 6H), 7.25 (d, J = 8.4 Hz, 6H), 2.52 (t, J = 11.2 Hz, 6H), 1.91–1.73 (m, 15H), 1.48–1.22 (m, 15H)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 145.5, 140.0, 138.0, 128.3, 127.2, 126.9, 126.5, 81.7, 44.2, 34.4, 26.9, 26.3; IR (KBr) 3563, 3440, 3023, 2923, 2854, 1913, 1612, 1496, 1450, 1396, 1319, 1188, 1157, 1002, 918, 818, 779, 540 cm^{-1}. Anal. Calcd for $C_{55}H_{58}O$: C, 89.87; H, 7.95. Found: C, 89.75; H, 8.09.

A mixture of crude tris(4′-cyclohexyl[1,1′-biphenyl]-4-yl)methanol (11.2 g), toluene (58 mL), and formic acid (25 mL) was refluxed for 12 h. The mixture was worked up as described for **4a**. The residue was recrystallized from CH_2Cl_2–hexane to afford **4b** (4.0 g, 46% yield/two steps) as a colorless amorphous solid.

4b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (t, J = 7.0 Hz, 12H), 7.27–7.22 (m, 12H), 5.62 (s, 1H), 2.55–2.51 (m, 3H), 1.92–1.84 (m, 12H), 1.77–1.74 (m, 3H), 1.49–1.36 (m, 12H), 1.30–1.23 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1, 142.6, 139.2, 138.3, 129.8, 127.2, 126.91, 126.89, 55.9, 44.2, 34.4, 26.9, 26.2; IR (KBr) 3422, 3023, 2923, 2849, 1905, 1496, 1447, 1398, 1261, 1108, 1005, 828, 812, 794, 776, 565, 535, 440, 409 cm^{-1}. Anal. Calcd for $C_{55}H_{58}$: C, 91.87; H, 8.13. Found: C, 91.63; H, 8.17.

Preparation of 5a,b from 4a,b. Representative Procedure. *7,7,7-Tris(4′-ethyl[1,1′-biphenyl]-4-yl)heptan-1-ol (**5a**).* n-BuLi (1.6 M solution in hexane, 1.25 mL, 2.0 mmol) was slowly added to the solution of tris(4-ethylbiphenyl)methane (0.56 g, 1 mmol) in 4.5 mL of dry THF with stirring at room temperature. The color of the solution turned to blue. 1-Chloro-6-(methoxymethoxy)hexane[18] (0.18g, 1 mmol) was added to the blue solution at room temperature, and the mixture was stirred for 12 h. MeOH (9 mL) and concd HCl

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(0.9 mL) were added to the mixture, and the mixture was heated at 60 °C for 1.5 h. Water was added, and the mixture was extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by silica gel column chromatography using hexane−AcOEt (4/1 (v/v)) as the eluent. Compound **5a** was isolated as a colorless amorphous solid (0.44 g, 67%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.0 Hz, 6H), 7.49 (d, J = 8.1 Hz, 6 H), 7.36 (d, J = 8.4 Hz, 6H), 7.24 (d, J = 8.0 Hz, 6H), 3.58 (q, J = 14 Hz, 2H), 2.67 (m, 8H), 1.49 (q, J = 15 Hz, 2H); 1.40−1.20 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 143.2, 138.4, 138.1, 129.6, 128.2, 126.8, 126.3, 63.0, 56.0, 40.4, 32.8, 30.2, 28.5, 25.7, 25.6, 15.5; IR (KBr) 3334, 3023, 2961, 2931, 2869, 1906, 1792, 1653, 1608, 1558, 1496, 1456, 1004, 815, 517 cm^{-1}. Anal. Calcd for $C_{49}H_{52}O$: C, 89.59; H, 7.98. Found: C, 89.33; H, 8.03.

5b: colorless amorphous solid: yield 0.28 g (49%, from 0.50 g (0.7 mmol) of **4b**); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (t, J = 8.0 Hz, 12H), 7.42 (d, J = 8.5 Hz, 6H), 7.30 (d, J = 8.5 Hz, 6H), 3.61 (t, J = 7.0 Hz, 2H), 2.69−2.66 (m, 2H), 2.59−2.54 (m, 3H), 1.96−1.88 (m, 12H), 1.81−1.78 (m, 3H), 1.54−1.24 (m, 23H) ; ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.0, 146.3, 138.4, 138.1, 129.5, 127.1, 126.8, 126.2, 62.9, 56.0, 44.2, 40.4, 34.4, 32.7, 30.2, 26.9, 26.1, 25.7, 25.6; IR (KBr) 3421, 3025, 2924, 2849, 2365, 2110, 1655, 1559, 1497, 1448, 1004, 813, 470, 438, 410 cm^{-1}. Anal. Calcd for $C_{61}H_{70}O$: C, 89.43; H, 8.61. Found: C, 89.32; H, 8.70.

Preparation of 6a,b from 5a,b. Representative Procedure. To a mixture of **5a** (1.64 g, 2.5 mmol), Ph_3P (1.31 g, 5.0 mmol), and imidazole (0.374 g, 5.5 mmol) in anhydrous ether/CH_3CN (7.5 mL/2.5 mL) was added I_2 (1.40 g, 5.5 mmol) with stirring at rt. After 2 h, the reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography using hexane−CH_2Cl_2 (3/1(v/v)) as the eluent to yield **6a** (1.80 g, 94%) as a colorless amorphous solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, J = 8.4 Hz, 6H), 7.50 (d, J = 8.7 Hz, 6H), 7.36 (d, J = 8.4 Hz, 6H), 7.24 (d, J = 8.7 Hz, 6H), 3.13 (t, J = 7.1 Hz, 2H), 2.67 (q, J = 7.5 Hz, 6H), 2.70−2.57 (m, 2H), 1.82−1.66 (m, 2H), 1.42−1.30 (m, 4H), 1.25 (t, J = 7.5 Hz, 9H), 1.26−1.10 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 143.2, 138.4, 138.0, 129.5, 128.2, 126.8, 126.3, 56.0, 40.3, 33.5, 30.4, 29.3, 28.5, 25.5, 15.6, 7.2; IR (KBr) 3022, 2962, 2928, 2869, 1903, 1496, 1005, 813 cm^{-1}. Anal. Calcd for $C_{49}H_{51}I$: C, 76.75; H, 6.70. Found: C, 77.00; H, 6.57.

6b: colorless amorphous solid: yield 0.47 g (96% from 0.44 g (0.53 mmol) of **5b**); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (t, J = 8.5 Hz, 12H), 7.35 (d, J = 8.0 Hz, 6H), 7.24 (d, J = 8.0 Hz, 6H), 3.12 (t, J = 7.0 Hz, 2H), 2.63−2.59 (m, 2H), 2.54−2.49 (m, 3H), 1.90−1.82 (m, 12H), 1.75−1.73 (m, 5H), 1.47−1.17 (m, 21 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1, 146.2, 138.5, 138.2, 129.5, 127.2, 126.8, 126.3, 56.0, 44.2, 40.4, 34.4, 33.5, 30.4, 29.3, 26.9, 26.2, 25.5, 7.15; IR (KBr) 3024, 2923, 2848, 2360, 1734, 1717, 1699, 1685, 1654, 1559, 1542, 1496, 1447, 1396, 1193, 1004, 812, 529, 472, 442, 418, 410 cm^{-1}. Anal. Calcd for $C_{61}H_{69}I$: C, 78.86; H, 7.49. Found: C, 78.71; H, 7.51.

General Procedure for the Template Synthesis of [2]-Rotaxanes (Table 1). To a solution of $Cu(CH_3CN)_4PF_6$ (37 mg, 0.1 mmol) in dry CH_2Cl_2 (5 mL) was added macrocyclic phenanthroline **7** (0.1 mmol), and the mixture was stirred at room temperature. After 5 min, the solution was added to a suspension of **8**[19] (0.1 mmol) in dry CH_3CN (5 mL), and the mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure. To the residue were added **6** (0.2 mmol), dry DMF (2 mL), and Cs_2CO_3 (130 mg, 0.4 mmol). The reaction mixture was stirred at 60 °C for 2 days, and then DMF was removed in vacuo. To the residue were added CH_3CN (10 mL), CH_2Cl_2 (5 mL), H_2O (5 mL), and KCN (33 mg, 0.5 mmol), and the mixture was stirred at room temperature for 14 h. The organic layer was washed with water, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography using hexane−CH_2Cl_2 as the eluent.

Rotaxane ***10a:*** pale yellow amorphous solid; yield 136 mg (60%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39−8.36 (br, 8H), 8.14 (d, J = 8.0 Hz, 2H), 8.11 (d, J = 8.4 Hz, 2H), 8.00−7.94 (br, 4H), 7.66 (s, 2H), 7.64 (s, 2H), 7.46 (d, J = 8.0 Hz, 12H), 7.45 (d, J = 8.4 Hz, 12H), 7.31 (d, J = 8.4 Hz, 12H), 7.19 (d, J = 8.0 Hz, 12H), 7.10 (t, J = 8.0 Hz, 1H), 7.03 (d, J = 7.2 Hz, 4H), 6.89 (d, J = 7.2 Hz, 4H), 6.70 (s, 1H), 6.46 (d, J = 8.0 Hz, 2H), 3.90−3.86 (m, 8H), 3.73 (t, J = 7.2 Hz, 4H), 2.64 (q, J = 7.6 Hz, 12H), 2.60−2.54 (m, 4H), 1.68−1.62 (m, 12H), 1.42−1.18 (m, 34H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 160.4, 160.3, 156.48, 156.2, 146.3, 143.1, 138.3, 138.0, 136.6, 132.4, 131.8, 129.8, 129.6, 129.0, 128.2, 127.4, 126.8, 126.2, 125.5, 125.4, 119.3, 114.8, 114.7, 106.8, 101.5, 68.0, 67.8, 56.0, 40.4, 31.6, 30.4, 29.7, 26.6, 29.5, 29.0, 28.5, 26.1, 25.9, 25.8, 25.6, 22.6, 15.5, 14.1; IR (KBr) 3432, 3023, 2931, 2861, 1905, 1604, 1489, 1419, 1396, 1304, 1250, 1173, 1149, 1119, 1011, 818, 741, 617 cm^{-1}; HR-MS (FAB-MS) calcd for $C_{164}H_{159}N_4O_6$ ([M + H]$^+$) 2280.2260, found 2280.2260. Anal. Calcd for $C_{164}H_{158}N_4O_6$: C, 86.35; H, 6.98; N, 2.46. Found: C, 86.28; H, 6.98; N, 2.31.

Rotaxane ***10b:*** colorless amorphous solid; yield 149 mg (64%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, J = 8.1 Hz, 4H), 8.40 (d, J = 8.4 Hz, 4H), 8.16 (d, J = 8.4 Hz, 2H), 8.11 (d, J = 8.4 Hz, 2H), 8.01 (d, J = 9.0 Hz, 2H), 7.94 (d, J = 8.4 Hz, 2 H), 7.64 (s, 2H), 7.62 (s, 2H), 7.47 (d, J = 8.1 Hz, 12H), 7.46 (d, J = 8.7 Hz, 12H), 7.32 (d, J = 8.7 Hz, 12H), 7.20 (d, J = 8.47 Hz, 12H), 7.12 (t, J = 8.1 Hz, 1H), 7.00 (d, J = 9.0 Hz, 4H), 6.95 (d, J = 8.7 Hz, 4H), 6.64 (s, 1H), 6.46 (d, J = 8.6 Hz, 2H), 3.88 (t, J = 6.0 Hz, 4H), 3.77 (t, J = 6.6 Hz, 4H), 3.68 (t, J = 6.6 Hz, 4H), 2.66 (q, J = 7.5 Hz, 12H), 2.59−2.50 (m, 4H), 1.72−1.40 (m, 16H), 1.37−1.19 (m, 8H), 1.24 (t, J = 7.5 Hz, 18 H), 1.19−0.99 (m, 16H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.5, 160.4, 165.4, 156.3, 156.2, 146.3, 146.0, 143.1, 138.3, 138.0, 136.6, 131.7, 129.8, 129.6, 128.9, 128.9, 128.3, 128.2, 127.4, 127.4, 126.8, 126.2, 125.5, 119.2, 114.7, 114.7, 106.7, 101.2, 67.8, 67.8, 55.9, 40.4, 30.3, 29.3, 29.3, 29.2, 28.5, 25.9, 25.9, 25.7, 25.5, 15.5; IR (KBr) 3024, 2929, 2855, 1903, 1602, 1587, 1494, 1249, 1173, 836, 816 cm^{-1}. Anal. Calcd for $C_{168}H_{166}N_4O_6$: C, 86.34; H, 7.16; N, 2.40. Found: C, 86.51; H, 7.12; N, 2.37.

Rotaxane ***10d:*** colorless amorphous solid; yield 132 mg (51%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (d, J = 8.5 Hz, 4H), 8.39 (d, J = 8.7 Hz, 4H), 8.15 (d, J = 8.5 Hz, 2H), 8.12 (d, J = 8.7 Hz, 2H), 8.00 (d, J = 8.7 Hz, 2H), 7.96 (d, J = 8.5 Hz, 2H), 7.67 (s, 2H), 7.64 (s, 2H), 7.46 −7.50 (m, 24H), 7.33 (d, J = 8.3 Hz, 12H), 7.23 (d, J = 8.5 Hz, 12H), 7.13 (t, J = 8.1 Hz, 1H), 7.06 (d, J = 8.5 Hz, 4H), 6.91 (d, J = 8 0.5 Hz, 4H), 6.73 (s, 1H), 6.48 (d, J = 8.3 Hz, 2H), 3.91−3.89 (m, 8H), 3.76 (t, J = 7.0 Hz, 4H), 2.66−2.53 (m, 10H), 1.88−1.59 (m, 42H), 1.50−1.27 (m, 50H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 160.4, 160.3, 156.5, 156.2, 146.9, 146.3, 145.9, 138.3, 138.1, 136.7, 131.9, 131.7, 129.8, 129.7, 129.5, 128.9, 127.4, 127.1, 126.9, 126.8, 126.7, 126.2, 125.5, 125.4, 119.4, 114.7, 114.6, 106.8, 101.5, 67.9, 67.7, 55.9, 44.2, 40.4, 34.4, 30.3, 29.7, 29.5, 29.4, 29.0, 26.9, 26.1, 26.0, 25.9, 25.8, 25.6; IR (KBr) 2923, 2849, 1602, 1587, 1489, 1248, 1173, 1004, 835, 813, 469 cm^{-1}; HR-MS (ESI-TOF) calcd for $C_{188}H_{196}N_4O_6$ ([M + 2H]$^{2+}$) 1302.7577, found 1302.7579.

Rotaxane ***10e:*** colorless amorphous solid; yield 143 mg (54%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71−8.41 (m, 8H), 8.17 (d, J = 8.5 Hz, 2H), 8.11 (d, J = 8.5 Hz, 2H), 8.03 (d, J = 8.5 Hz, 2H), 7.96 (d, J = 8.5 Hz, 2H), 7.65 (s, 2H), 7.63 (s, 2H), 7.52−7.48 (m, 24H), 7.34 (d, J = 8.5 Hz, 12H), 7.24 (d, J = 8.3 Hz, 12H), 7.15 (t, J = 8.1 Hz, 1H), 7.03 (d, J = 8.7 Hz, 4H), 6.98 (d, J = 8 0.7 Hz, 4H), 6.68 (s, 1H), 6.50 (d, J = 8.3 Hz, 2H), 3.91 (t, J = 6.2 Hz, 4H), 3.79 (t, J = 6.4 Hz, 4H), 3.70 (t, J = 6.6 Hz, 4H), 2.61−2.48 (m, 10H), 1.88−1.68 (m, 30H), 1.51−1.35 (m, 70H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 160.4, 160.4, 156.3, 156.1, 146.9, 146.3, 145.9, 138.3, 138.1, 136.6, 131.6, 129.8, 129.5, 128.9, 127.3, 127.1, 126.7, 126.2, 125.4, 119.1, 114.7, 114.6, 106.7, 101.3, 67.8, 67.7, 55.9, 44.1, 40.4, 34.4, 30.2, 29.3, 29.2, 29.1, 26.8, 26.1, 25.9, 25.8, 25.7, 25.5; IR (KBr) 2923, 2849, 1602, 1587, 1489, 1248, 1173, 1004, 835, 813, 469 cm^{-1}; HR-MS (ESI-TOF) calcd for $C_{192}H_{204}N_4O_6$ ([M + 2H]$^{2+}$) 1330.7890, found 1330.7916.

11a: colorless amorphous solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (d, J = 8.7 Hz, 4H), 8.22 (d, J = 8.4 Hz, 2H), 8.04 (d, J = 8.4 Hz, 2H), 7.71 (s, 2H), 7.50 (d, J = 8.1 Hz, 24H), 7.38 (d, J = 8.4 Hz, 12H), 7.23 (d, J = 8.7 Hz, 12H), 7.04 (d, J = 8.7 Hz, 4H), 4.00 (t, J = 6.3 Hz, 4H), 2.66 (q, J = 7.5 Hz, 12H), 2.70−2.62 (m, 4H), 1.83−1.70 (m, 4H), 1.52−1.37 (m, 8H), 1.25 (t, J = 7.5 Hz, 18H), 1.30−1.17 (m,

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4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5 156.4, 146.3, 145.8, 143.2, 138.4, 138.0, 136.9, 131.7, 129.6, 129.0, 128.2, 127.5, 126.8, 126.3, 125.6, 119.5, 114.7, 68.0, 56.0, 40.4, 30.2, 29.3, 28.5, 26.0, 25.7, 15.5; IR (KBr) 3023, 2960, 2930, 2867, 1902, 1602, 1495, 1248, 1173, 1005, 815 cm^{-1}. Anal. Calcd for $C_{122}H_{116}N_2O_2$: C, 89.23; H, 7.12; N, 1.71. Found: C, 89.53; H, 7.18; N, 1.69.

11b: colorless amorphous solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, J = 9.0 Hz, 4H), 8,22 (d, J = 8.5 Hz, 2H), 8.06 (d, J = 9.0, 2H), 7.71 (s, 2H), 7.54−7.52 (m, 24H), 7.40(d, J = 8.5 Hz, 12H), 7.26 (d, J = 8.5 Hz, 12H), 7.08 (d, J = 9.0 Hz, 4H), 4.02 (t, J = 6.5 Hz, 4H), 2.70−2.67 (m, 4H), 2.55−2.50 (m, 6H), 1.92−1.74 (m, 34H), 1.49−1.22 (m, 42H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 156.3, 147.0, 146.3, 146.0, 138.4, 138.2, 136.7, 131.9, 129.6, 128.9, 127.4, 127.2, 126.8, 126.3, 125.5, 119.2, 114.7, 67.9, 56.0, 44.2, 40.4, 34.4, 30.2, 29.3, 26.9, 26.1, 25.9, 25.7; IR (KBr) 3024, 2923, 2848, 1736, 1603, 1495, 1447, 1247, 1173, 1004, 836, 812, 732, 528, 439 cm^{-1}. Anal. Calcd for $C_{146}H_{152}N_2O_2$: C, 89.16; H, 7.79; N, 1.42. Found: C, 88.91; H, 7.98; N, 1.38.

Deslipping Reactions of [2]Rotaxanes (Table 2). A solution of the rotaxane (1 μmol) in 1,1,2,2-tetrachloroethane-d_2 (0.6 mL) was heated in an NMR tube. The ratio of the starting material and the axle was monitored by the integration of the NMR signals (rotaxane (**10a**,**b**,**e**): 3.7−3.95 ppm, dissociated compounds (**7a**,**b** and **11a**,**b**): 3.95−4.1 ppm). Heating was continued until 50−60% of the rotaxane dissociated. The kinetic parameters were calculated by carrying out these reactions at different temperatures.

Alkyne ***13.*** To a solution of **6b** (0.65 g, 0.7 mmol) and 2-(4-hydroxyphenyl)-1-trimethylsilylacetylene[20] (**12**, 0.26 g, 1.4 mmol) in DMF (10 mL) was added K_2CO_3 (1.0 g, 7.0 mmol) with stirring. The mixture was heated to 60 °C and stirred for 14 h. Then DMF was removed in vacuo. To the residue were added THF (5 mL), MeOH (5 mL), KF (1.0 g), and KOH (0.04 g). After being stirred at 60 °C for 19 h, the mixture was cooled to room temperature and acidified with 2 M aqueous HCl to pH 2. The aqueous layer was extracted with CH_2Cl_2, and the organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography using hexane−CH_2Cl_2 (6/1 (v/v)) to afford **13** (0.52 g, 82%) as a colorless amorphous solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52−7.47 (m, 12H), 7.38−7.33 (m, 8H), 7.26−7.22 (m, 6H), 6.77 (d, J = 9.0 Hz, 2H), 3.88 (t, J = 6.4 Hz, 2H), 2.96 (s, 1H), 2.65−2.48 (m, 5H), 1.87−1.71 (m, 18H), 1.50−1.22 (m, 20H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 147.1, 146.3, 138.4, 138.2, 133.5, 129.6, 127.2, 126.8, 126.3, 120.3, 114.4, 83.8, 75.6, 67.9, 56.0, 44.2, 40.4, 34.4, 30.1, 29.1, 26.9, 26.2, 25.9, 25.6; IR (KBr) 3284, 3024, 2923, 2849, 1605, 1496, 1447, 1248, 1004, 812, 534 cm^{-1}. Anal. Calcd for $C_{69}H_{74}O$: C, 90.15; H, 8.11. Found: C 89.97; H, 8.11.

General Procedure for the Synthesis of [2]Rotaxanes by Oxidative Coupling Reactions of Alkynes. To a mixture of macrocyclic phenanthroline−Cu(I) complex **14** (0.02 mmol), alkyne **13** (74 mg, 0.08 mmol), and K_2CO_3 (0.017g, 0.12 mmol) in dry xylene (1.0 mL) was added I_2 (10 mg, 0.04 mmol) with stirring. The mixture was heated to 130 °C and stirred for 48 h. CH_3CN (3 mL), CH_2Cl_2 (3 mL), KCN (10 mg, excess), and H_2O (2 mL) were added, and the mixture was stirred at room temperature for 4 h. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layer was washed with water. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography using hexane−CH_2Cl_2 (3/1 (v/v)) as the eluent and preparative GPC to afford rotaxane **15.**

Rotaxane 15a: colorless amorphous (41 mg, 82%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, J = 8.5 Hz, 4H), 8.17 (d, J = 8.2 Hz, 2H), 8.00 (d, J = 8.5 Hz, 2H), 7.67 (s, 2H), 7.50 −7.46 (m, 24H), 7.41 (d, J = 8.9 Hz, 2H), 7.32 (d, J = 8.5 Hz, 12H), 7.24−7.22 (m, 12H), (t, J = 8.2 Hz, 1H), 6.98 (d, J = 8.9 Hz, 4H), 6.73 (d, J = 8 0.9 Hz, 4H), 6.63 (s, 1H), 6.47 (d, J = 8.3 Hz, 2H), 3.95−3.89 (m, 8H), 3.77 (t, J = 6.4 Hz, 4H), 2.58−2.49 (m, 10H), 1.90−1.73 (m, 28H), 1.62−1.57 (m, 4H), 1.47−1.13 (m, 50H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 160.4, 159.7, 156.3, 147.0, 146.2, 138.4, 138.1, 136.7, 134.0, 131.7, 129.7, 129.5, 128.9, 127.4, 127.1, 127.0, 126.9, 126.8, 126.2, 125.5, 119.2, 114.8, 114.7, 113.5, 107.1, 100.9, 81.6, 73.3, 67.9, 67.8, 67.7, 55.9, 44.2, 40.4, 34.4, 30.1, 29.6, 29.1, 26.9, 26.1, 25.9, 25.8, 25.7, 25.6; IR (KBr) 3025, 2922, 2849, 1601, 1495, 1447, 1286, 1248, 1170, 1004, 833, 532 cm^{-1}; HR-MS (MALDI-TOF) calcd for $C_{180}H_{189}N_2O_6$ ([M + H]$^+$) 2474.4540, found 2474.4662.

Rotaxane 15b: colorless amorphous (37 mg, 74%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (d, J = 8.9 Hz, 4H), 8.17 (d, J = 8.5 Hz, 2H), 8.00 (d, J = 8.5 Hz, 2H), 7.67 (s, 2H), 7.50−7.45 (m, 24H), 7.39 (d, J = 8.9 Hz, 4H), 7.39 (d, J = 8.5 Hz, 12H), 7.25−7.22 (m, 12H), 7.10 (t, J = 8.1 Hz, 1H), 7.01 (d, J = 8.9 Hz, 4H), 6.72 (d, J = 8 0.9 Hz, 4H), 6.51 (s, 1H), 6.44 (d, J = 8.3 Hz, 2H), 3.93−3.86 (m, 8H), 3.78 (t, J = 6.4 Hz, 4H), 2.59−2.47 (m, 10H), 1.88−1.57 (m, 40H), 1.50−1.13 (m, 60H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 160.4, 159.7, 156.1, 147.0, 146.3, 138.4, 138.1, 134.0, 129.7, 129.5, 129.0, 127.4, 127.2, 126.8, 126.2, 125.5, 114.8, 114.6, 113.6, 106.9, 100.8, 81.5, 73.2, 68.0, 67.9, 67.8, 67.7, 56.0, 44.2, 40.4, 34.4, 30.2, 29.7, 29.3, 29.3, 29.2, 29.1, 26.9, 26.2, 25.9, 25.8, 25.7, 25.6; IR (KBr) 3025, 2923, 2849, 1602, 1496, 1249, 1170, 1004, 813, 531 cm^{-1}; HR-MS (MALDI-TOF) calcd for $C_{184}H_{197}N_2O_6$ ([M + H] $^+$) 2530.5166, found 2530.507.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra (^{1}H, ^{13}C) for new compounds and details of the kinetic experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(3) Most of the rotaxanes described in this paper are "pseudorotaxanes", which are metastable and dissociate under certain conditions. We suspect, however, that a significant number of "rotaxanes" reported to date are "psudorotaxanes", since the detailed study of the dissociation reaction under harsh conditions has not been carried out for many compounds. Therefore, we described our compounds as "rotaxanes". It may be necessary to utilize kinetic parameters for the

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(6) During the purification, no significant change of the product distribution was observed (TLC analyses).

(7) We confirmed the increased thermal stability of **10b** compared to **1b** by kinetic experiments (vide infra).

(8) NMR analyses of the crude products indicated that the alkylation of **9** proceeded in the reactions reported in Table 1.

(9) The dissociation of the rotaxane could be easily monitored, since the chemical shifts of the rotaxanes and the dissociated components are significantly different. See ref 4m and the Supporting Information.

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