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Synthesis and Shuttling Behavior of [2]Rotaxanes with a Pyrrole Moiety

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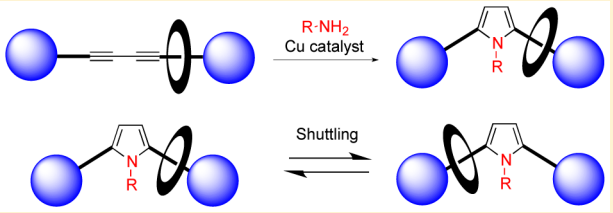
Supporting Information

ABSTRACT: We synthesized [2]rotaxanes with a pyrrole moiety from a [2]rotaxane with a 1,3-diynyl moiety. The conversion of the 1,3-diynyl moiety of the axle component to the pyrrole moiety was accomplished by a Cu-mediated cycloaddition of anilines. The cycloaddition reaction was accelerated when the [2]rotaxane was used as the substrate. The effect of the structure of the pyrrole moiety on the rate of the shuttling was studied.



INTRODUCTION

[2]Rotaxane is an interlocked compound that is composed of a ring component and an axle component.[1] The presence of bulky blocking groups at both ends of the axle component prevents the dissociation of the two components. The ring component could move freely along the axle or it could be located in a specific position where the favorable interaction between the two components exists. The position is referred to as a binding site, a recognition site, or a station. When two stations are present in an axle component, the ring component could move between the two stations (Figure 1a). This phenomenon is called shuttling. The shuttling behavior of the two-station [2]rotaxane has been an attractive subject for chemists.[2] The shuttling could be initiated by various stimuli, and the rate of the shuttling could be controlled by the introduction of a substituent as a kinetic molecular barrier[3] between the two stations (Figure 1b). Since control of the shuttling process is critical for the development of molecular switches and ratchets, the relationship between the structure of the [2]rotaxane and the rate of the shuttling process has been studied by several groups.[4] For example, Stoddart and co-workers studied the effect of the structure of the spacer units on the rate of the shuttling process.[4a] The effect of the flexibility or the length of the axle component on the rate of the shuttling has been studied thoroughly by Hirose and co-workers.[4f]

In the shuttling of the two-station [2]rotaxane, the kinetic barrier between the two stations is the sum of (a) the energy required for the release of the ring component from the station and (b) the energy required for the ring component to pass through the kinetic molecular barrier (Figure 1b). It is therefore difficult to separate these two factors and discuss the relationship between the structure of the kinetic molecular barrier and the activation energy of the shuttling process. In order to quantitatively estimate the effect of the kinetic molecular barrier, it is desirable to synthesize a "partitioned" [2]rotaxane (Figure 1c). In the partitioned [2]rotaxane, the rate of the movement of the ring component between the sections was controlled only by the presence of the kinetic molecular barrier. The ring component moves freely within the section, which is divided by the kinetic molecular barrier.

We have been interested in the chemistry of interlocked compounds and synthesized a series of [2]rotaxanes with 1,3-diynyl moiety in the axle component.[5] In this paper, we report the synthesis of partitioned [2]rotaxanes with an *N*-substituted pyrrole moiety that acts as the kinetic molecular barrier. We carried out the quantitative analysis of the shuttling process and disclosed the relationship between the structure of the kinetic molecular barrier and the rate of the shuttling process.

RESULTS AND DISCUSSION

Synthesis of [2]Rotaxanes with Pyrrole Moiety. The reaction of 1,3-diyne with amine is a unique method for the synthesis of pyrroles.[6] This reaction was catalyzed by CuCl or other metals. It has been postulated that the reaction proceeded by the nucleophilic attack of the amine on the 1,3-diynyl moiety, and this process would be accelerated by the coordination of CuCl to the diynyl moiety. We utilized this reaction to convert the 1,3-diynyl moiety of a [2]rotaxane (**1**)[6e] to the corresponding pyrrole (Scheme 1). Compound **1** was treated with an excess of aniline (**2a**, 20 equiv) in the presence of CuCl (1.0 equiv) at 120 °C for 2 h, and formation of the pyrrole was observed. After the removal of the Cu salt by the addition of aqueous ammonia,[7] the [2]rotaxane **3a** was isolated

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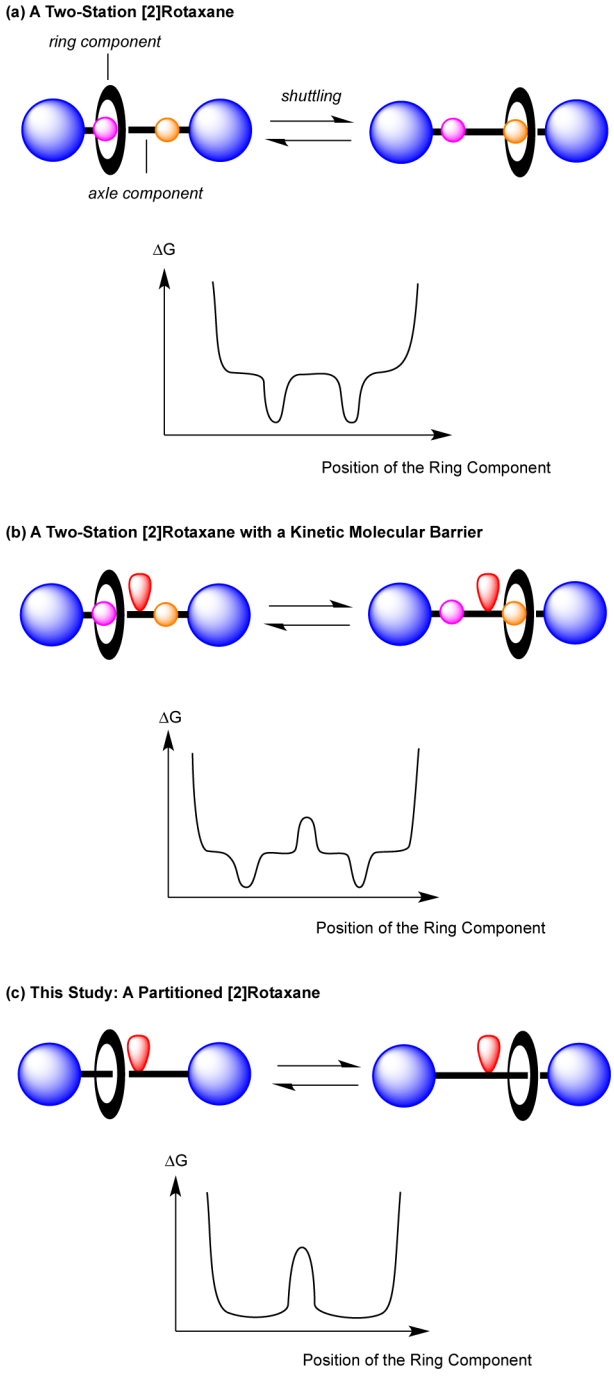
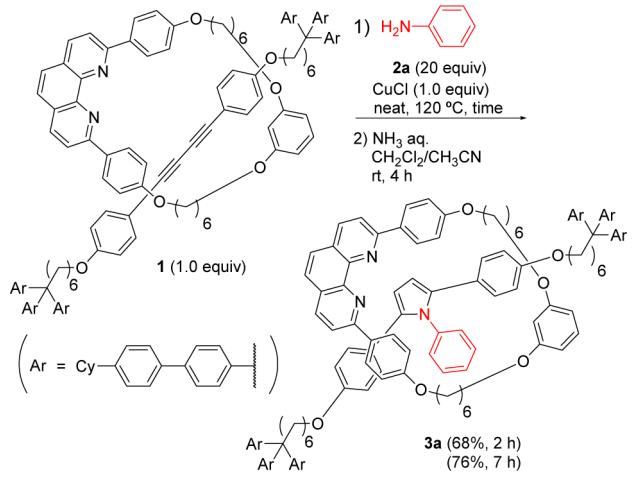


Figure 1. Shuttling behavior of [2]rotaxanes.

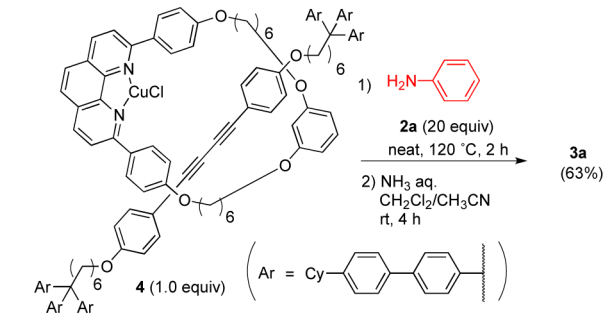
in 68% yield (Scheme 1). When the reaction time was extended to 7 h, the yield of **3a** increased to 76%. Although we initially expected that the reactivity of the 1,3-diynyl moiety in **1** would be low due to the presence of the macrocyclic phenanthroline as a "protective group",[8] the result indicated that the 1,3-diynyl moiety of **1** was sufficiently reactive.

In order to understand the observed high reactivity, we carried out a series of control experiments. The results are summarized in Scheme 2 and Table 1. The rate of the reaction of **1** was comparable to that of the [2]rotaxane–CuCl complex (**4**): when the reaction of **4** with **2a** was carried out under similar reaction conditions, **3a** was isolated in 63% yield.[9] The observed results could be explained by the facile formation of **4**

Scheme 1. Synthesis of a [2]Rotaxane with Pyrrole Moiety



Scheme 2. Synthesis of a [2]Rotaxane from [2]Rotaxane–CuCl Complex 4



from **1** and CuCl in situ under the reaction conditions described in Scheme 2.

We next studied the reactivity of **5**, which is the axle component of **4**, in the presence of various copper catalysts (Table 1). The reaction of **5** with **2a** (20 equiv) was carried out in the presence of CuCl at 120 °C for 2 h, and the corresponding pyrrole **6** was isolated in low yield (16%, entry 1). When the reaction was carried out for a longer period (24 h), the yield of **6** increased to 78%, indicating that the low yield of **6** observed in entry 1 is due to the low catalytic activity of CuCl under the reaction conditions (entry 2). When a phenanthroline–CuCl complex (**7**) was used as the catalyst, the yield of **6** was low (entry 3). The catalytic activity of the macrocyclic phenanthroline–CuCl complex (**8**) turned out to be much lower compared to that of CuCl or **7**, and only a trace amount of **6** was detected in the reaction mixture (entry 4). The observed high reactivity of **4** as well as **1** in the synthesis of the pyrrole could be explained by the intramolecular activation of the 1,3-diynyl moiety. Since the copper ion was located in the proximity of the axle component, the addition of the amine to the 1,3-diynyl moiety would be accelerated (Scheme 3). This type of activation has been reported in some reactions where the substrate was threaded through the macrocyclic catalyst.[10]

In order to study the effect of the structure of the pyrrole moiety on the shuttling behavior of the [2]rotaxane, a series of [2]rotaxanes was synthesized by the reaction of **1** with amines. The results are summarized in Table 2. The reaction of **1** with *p*-cyclohexylaniline **2b** proceeded in the presence of CuCl under similar reaction conditions, and the product was isolated in 74% yield (entry 2). We also succeeded in the introduction

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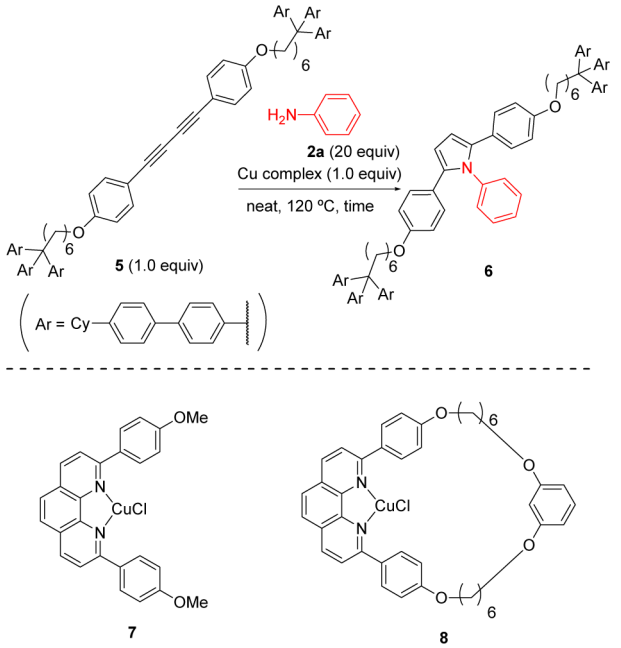
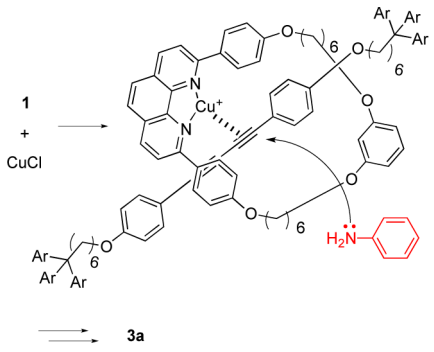
Table 1. Reaction of 5 with Aniline 2a in the Presence of Cu Complexes



entry	time (h)	Cu complex	yield (%)
1	2	CuCl	16
2	24	CuCl	78
3	2	**7**	25
4	2	**8**	trace

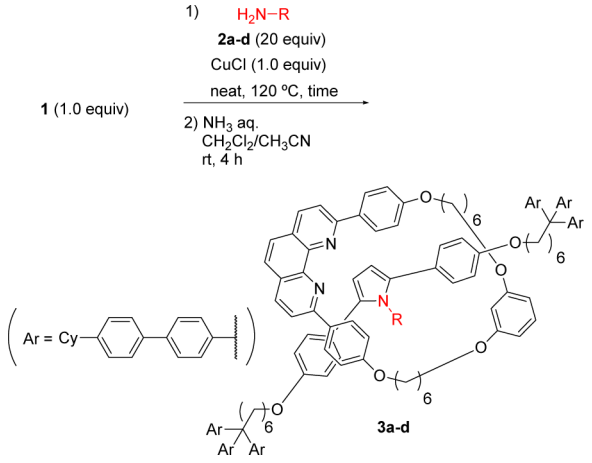
Scheme 3. Proposed Mechanism for the Cu-Mediated Reaction of 1 with Anilines

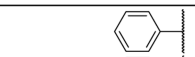
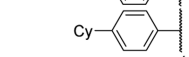
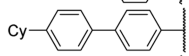


of a larger substituent to the [2]rotaxane: the reaction of **1** with *p*-(4-cyclohexylphenyl)aniline **2c** proceeded under similar reaction conditions, and the coupling product was isolated in 71% yield (entry 3). Compared to the reaction of **1** with **2a**–**c**, the reaction of **1** with an aliphatic amine (**2d**) was sluggish. The corresponding [2]rotaxane (**3d**) was isolated in lower yield (42%) compared to other [2]rotaxanes (entry 4).[11]

^{1}H NMR Spectra of [2]Rotaxanes. ^{1}H NMR spectra of the [2]rotaxanes (**3a**–**d**) indicated that the shuttling process was affected by the structure of the substituents introduced at the pyrrole moiety. The ^{1}H NMR spectra of the [2]rotaxanes were compared, and the results are summarized in Figure 2. In the NMR spectrum of **1**, sharp signals were observed and the signals of the two blocking groups (two tris(4-cyclohexylbiphenyl)methyl groups) were equivalent. Four strong doublets, which appeared at 7.2–7.5 ppm, were assigned as the signals of the aromatic protons of the two blocking

Table 2. Synthesis of Various [2]Rotaxanes with Pyrrole Moiety



entry	amine	R	time (h)	product	yield (%)
1	**2a**		7	**3a**	76
2	**2b**		7	**3b**	74
3	**2c**		7	**3c**	71
4	**2d**		120	**3d**	42

groups. The observed results could be explained by the fast movement of the ring moiety along the axle in the NMR time scale: if the shuttling of the ring moiety were slow, the signals of the blocking group would be nonequivalent, and eight doublets would be observed. Compared to the NMR spectrum of **1**, the broadening of some signals was observed in the NMR spectrum of **3a**. In particular, the signals appeared at 6.5–7.5 ppm, which should correspond to the signals of the aromatic protons of the axle component, were broad and the assignment of the signals was difficult. The broadening was also observed in the NMR spectrum of **3d**.

On the other hand, no broadening was observed in the NMR spectrum of **3b** or **3c**. Compared to the NMR spectrum of **1**, the number of the signals observed in the spectra of **3b** and **3c** significantly increased. In order to understand the observed results, we compared the NMR spectrum of **3b** with **9**, which corresponds to the axle moiety of **3b** (Figure 3). As expected, the two blocking groups of **9** were magnetically equivalent, and four doublets (H^a–H^d), which were assigned as the signals of the aromatic protons of the blocking groups, were observed at 7.2–7.5 ppm. Other aromatic protons (H^e and H^f) also appeared as doublets (6.65 and 6.99 ppm), and the protons of the pyrrole moiety (H^g) appeared as a singlet (6.36 ppm). In contrast, the detailed analysis of the spectrum of **3b** indicated that the two blocking groups of **3b** were nonequivalent. For example, a doublet, which was observed at 7.51 ppm, was assigned as H^c in the NMR spectrum of **9**. In the NMR spectrum of **3b**, two doublets (7.50 and 7.43 ppm), which correspond to the signals of H^c and $H^{c'}$, respectively, were observed. It is noteworthy that the chemical shift of one doublet observed in **3b** is similar to that of the doublet observed in **9**, and the other doublet shifted to the higher field. Similar change was observed in other protons (H^a, H^b, and H^d).

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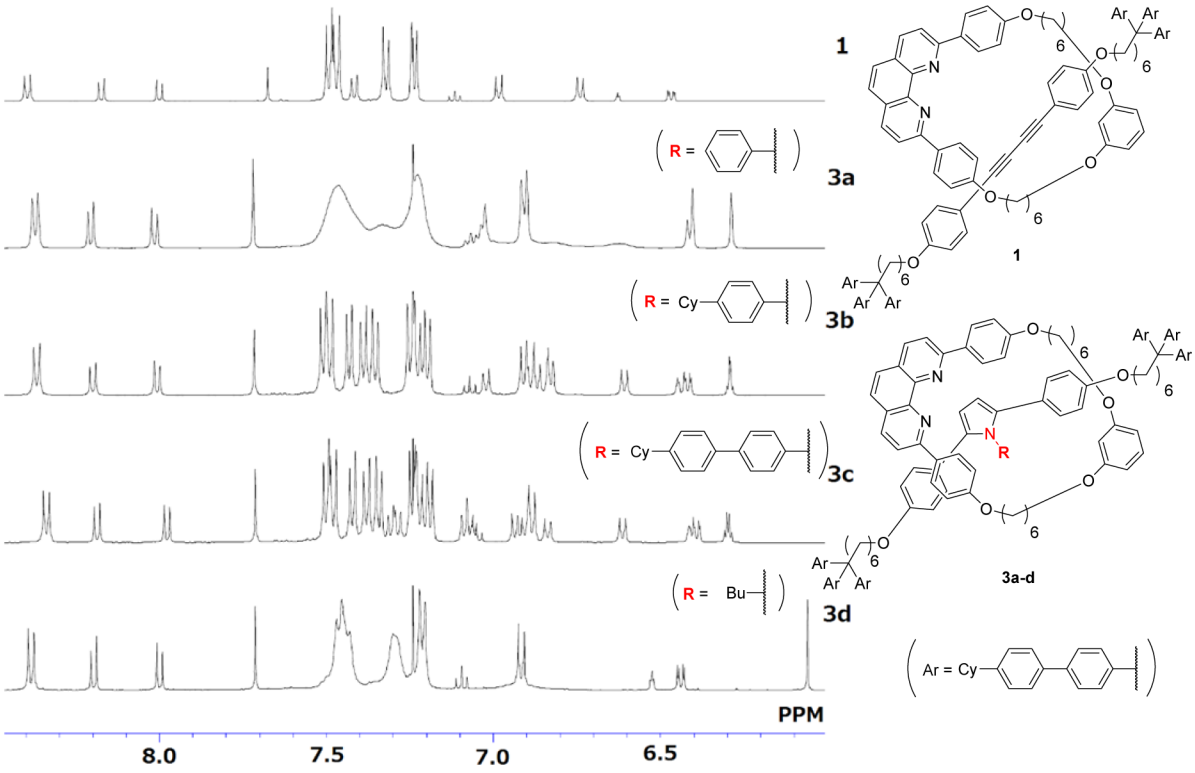

Figure 2. ^{1}H NMR spectra of **1** and **3a–d** (500 MHz, 297 K, $CDCl_3$).

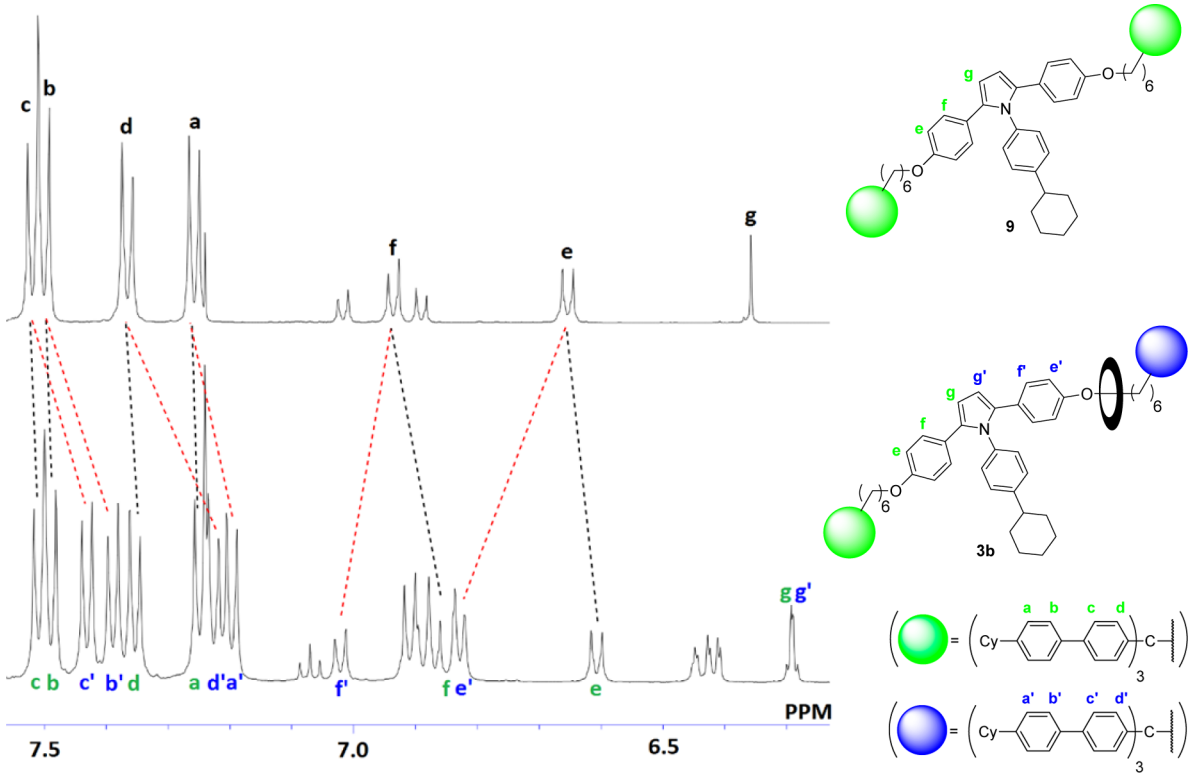

Figure 3. Comparison of the ^{1}H NMR spectra of **3b** and **9** (500 MHz, 297 K, $CDCl_3$).

The splitting of the signals was also observed in other aromatic protons incorporated in the axle component (H^e and H^f). Though the observed difference of the chemical shifts was small, the protons bound to the pyrrole ring (H^g and $H^{g'}$ at 6.30 ppm) were nonequivalent. The difference of the NMR spectra of **9** and **3b** could be explained by the inhibited movement of the ring component between the sections of the axle moiety of **3b** divided by the pyrrole ring. On the NMR time scale, the ring component resides in one section. In the NMR spectrum of **3b**, the chemical shifts of one blocking group

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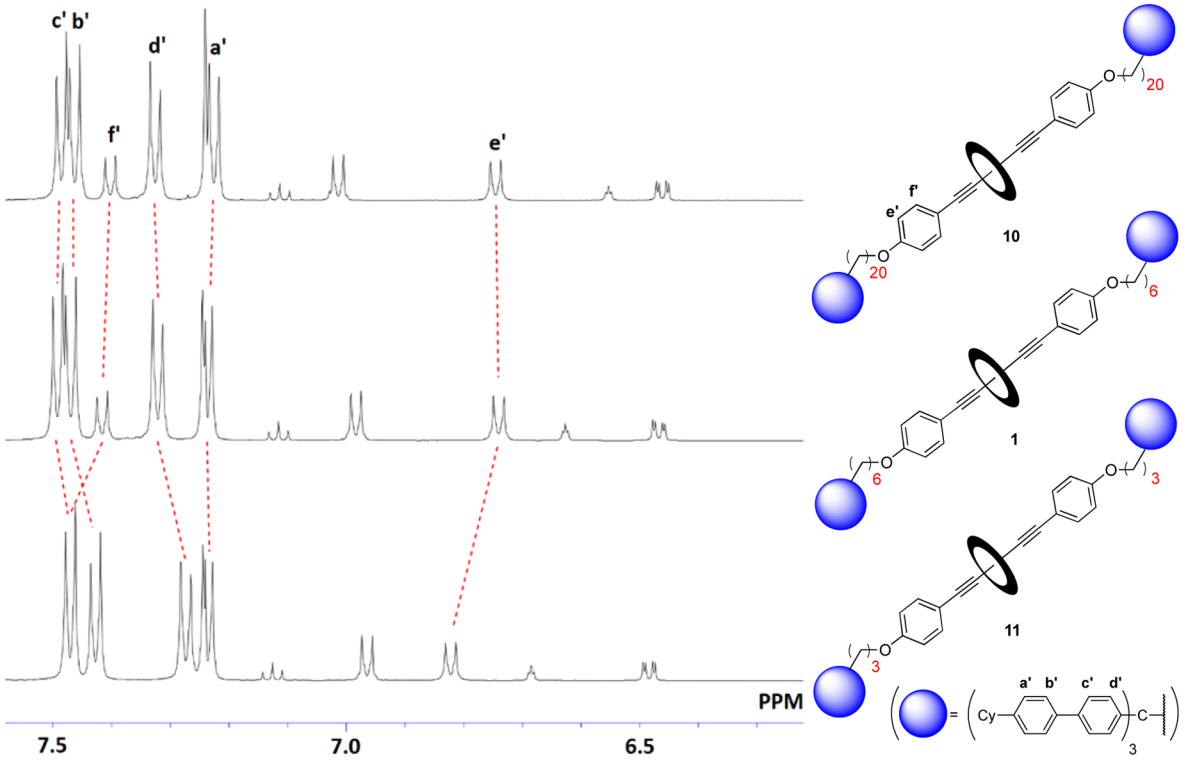

Figure 4. Comparison of the ^{1}H NMR spectra of **1**, **10**, and **11** (500 MHz, 297 K, $CDCl_3$).

($H^{a'}$–$H^{d'}$) would be influenced by the presence of the ring moiety in the proximity, and the chemical shifts of $H^{a'}$–$H^{d'}$ would be different from those of H^a–H^d observed in **9**. The other blocking group of **3b** would be much less affected by the presence of the ring moiety at the other section, and the chemical shifts of H^a–H^d in **3b** would be similar to those observed in **9**. The assignment of the signals of **3b** was based on the above-mentioned assumption. The difference of the chemical shifts of the blocking groups observed in the ^{1}H NMR spectrum of **3b** indicated that the presence of the ring component in the proximity of the blocking group would induce the high-field shift of the signals. We confirmed this by comparing the chemical shifts of a series of [2]rotaxanes. The results are summarized in Figure 4. We compared the NMR spectra of [2]rotaxanes **10**,[12] **1**, and **11**. Compound **10** is a [2]rotaxane with a very long axle moiety, which is composed of C20 alkylene chain. The length of the alkylene chain was shorter in **1**, and very short alkylene groups (propylene groups) were introduced to rotaxane **11**. The difference of the NMR spectra of **10** and **1** was very small. On the other hand, the chemical shifts of the blocking group of **11** (7.2–7.5 ppm) were different from those of **1**. For example, the signal of $H^{d'}$, which was observed as a doublet at 7.32 ppm in the NMR spectrum of **1**, shifted to 7.27 ppm in the NMR spectrum of **11**. The high-field shifts of other signals ($H^{a'}$, $H^{b'}$, and $H^{c'}$) were also observed. These results strongly imply that the high-field shift of the signals of the blocking group would be observed when the ring moiety is located in the proximity of the blocking group and justify the assignment of the NMR spectrum of **3b**. The NMR spectrum of **3c** would be explained similarly.

We confirmed that the shuttling in **3b** and **3c**, which are rotaxanes with bulky kinetic molecular barriers, is very slow on the NMR time scale. Compared to the substituents which were introduced as the kinetic molecular barrier to **3a** and **3d**, the size of the substituents introduced to **3b** and **3c** are larger. Therefore, the rate of the shuttling process of **3a** and **3d** would decrease. The observed NMR spectra of **3a** and **3d** would reflect the slow movement of the ring component between the sections divided by the pyrrole moiety on the NMR time scale.

In order to study the shuttling behavior in detail, the VT ^{1}H NMR of **3a** was examined (Figure 5). The NMR spectrum of **3a** was sharp in $CDCl_3$ at low temperature (233 K). Due to the reduced rate of the shuttling, the nonequivalent signals of the stopper moiety (H^a–H^d and $H^{a'}$–$H^{d'}$) and *p*-alkoxyphenyl moiety (H^e and $H^{e'}$) were observed. The observed spectrum was similar to the NMR spectrum of **3b** at rt (297 K, Figure 2). At higher temperature (273–323 K), the broadening of the signals (H^e and $H^{e'}$) was observed. Two signals (H^e and $H^{e'}$) merged, and they were observed as a broad signal at 313 K. On the basis of the analysis of the signals of the *p*-alkoxyphenyl moiety (H^e and $H^{e'}$), the energy barrier for the shuttling of **3a** was estimated to be 14.7 ± 0.2 kcal/mol at 298 ± 2 K in $CDCl_3$ and 15.5 ± 0.1 kcal/mol at 323 ± 1 K in $(CDCl_2)_2$ (Table 3, entries 1 and 2). Similar VT ^{1}H NMR experiments were carried out for **3d**, and the energy barrier for the shuttling of **3d** was estimated to be 13.1 ± 0.3 kcal/mol at 278 ± 5 K in $CDCl_3$ (entry 3).[13,14] We confirmed that the shuttling in **1** was very fast on the NMR time scale: the signals of the two dumbbell moieties were magnetically equivalent, and no broadening of the NMR signals was observed at 213 K in $CDCl_3$. In contrast, the shuttling in **3b** or **3c** was very slow. Even at 393 K (in $(CDCl_2)_2$), no broadening of the NMR signals was observed, and the two dumbbell moieties were magnetically non-equivalent.[13] The result indicated that the shuttling of the ring component between the two sections was strongly inhibited due to the presence of a bulky kinetic molecular barrier introduced to **3b** or **3c**. The activation energy ($\Delta G^{\ddagger}$) for

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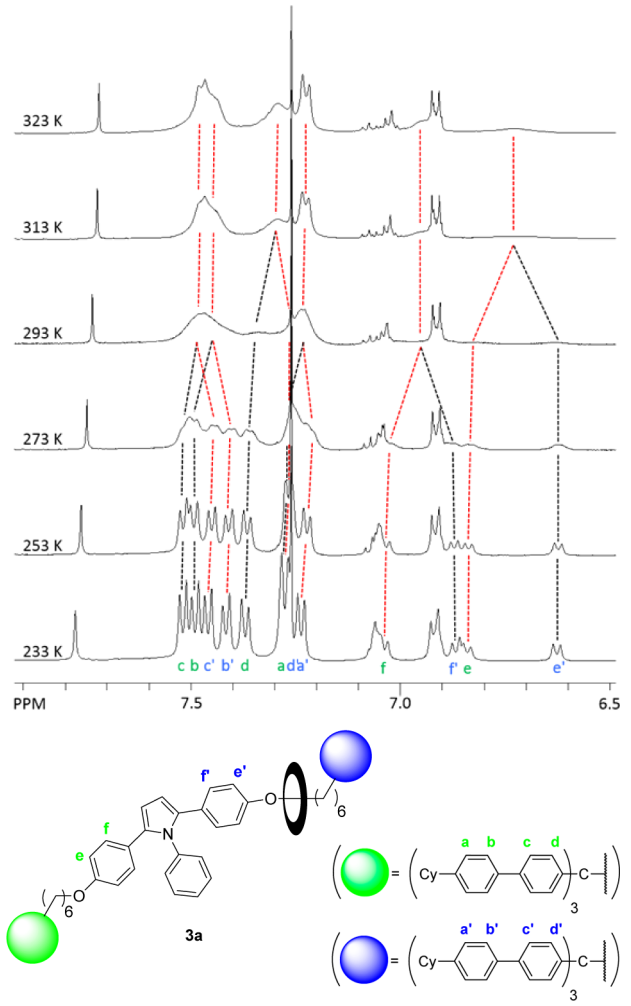

Figure 5. VT ^{1}H NMR spectra of **3a** (500 MHz, $CDCl_3$).

Table 3. Kinetic Parameters for the Shuttling of [2]Rotaxanes

entry	rotaxane	solvent	coalescence temp (K)	$\Delta G^{\ddagger}$ (kcal/mol)
1	**3a**	$CDCl_3$	308 ± 2	14.7 ± 0.2
2	**3a**	$(CDCl_2)_2$	325 ± 1	15.5 ± 0.1
3	**3d**	$CDCl_3$	278 ± 5	13.1 ± 0.3

the shuttling of **3b** or **3c** was estimated to be larger than 20 kcal/mol.

In summary, we synthesized a series of [2]rotaxanes with pyrrole moiety from a [2]rotaxane with 1,3-diynyl moiety by Cu-mediated cycloaddition reaction. The cycloaddition reaction was accelerated by the presence of the Cu species in the proximity of the 1,3-diynyl moiety of the [2]rotaxane. The relationship between the size of the kinetic molecular barrier and the rate of the shuttling was quantitatively analyzed. The study would contribute to the understanding of the chemistry of [2]rotaxane and provide valuable information for the design of molecular switches and ratchets.

EXPERIMENTAL SECTION

General Information. Reagents were commercially available and used without further purification unless otherwise noted. Compounds **1**,[5b] **5**,[15] **10**,[12] **12**,[5b] **13**,[16] **14**,[5a] **15**,[5a] **16**,[17] **18**,[18] and **21**[5a] were prepared by the reported procedure. Chemical shifts were reported in delta units (δ) relative to chloroform (7.24 ppm for ^{1}H NMR and 77.23 ppm for ^{13}C NMR). Multiplicity was indicated by s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), or m (multiplet). Coupling constants, *J*, are reported in hertz. 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).

*p-(4-Cyclohexylphenyl)aniline (**2c**).*[19] A reported procedure[20] was generally followed to synthesize **2c**. A mixture of 4-bromocyclohexylbiphenyl (**12**) (1.9 g, 60 mmol, 1.0 equiv), Cu_2O (0.086 g, 0.60 mmol, 0.010 equiv), aqueous ammonia (30% solution, 8.4 mL, 120 mmol, 20 equiv), and NMP (8.4 mL, 120 mmol, 20 equiv) was stirred at 100 °C in a sealed tube under Ar atmosphere. After 39 h, the solution was cooled at room temperature, quenched with water, and extracted with CH_2Cl_2. The combined organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography using hexane/ethyl acetate (10/1 (v/v)) to afford **2c** (0.91 g, 36 mmol, 60%) as a white powder. Mp: 101.0−101.5 °C (lit.[19] mp 102 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.47 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 2H), 3.67 (br s, 2H), 2.53 (t, *J* = 10.0 Hz, 1H), 1.96−1.72 (m, 5H), 1.51−1.22 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.3, 145.7, 138.8, 131.8, 128.0, 127.3, 126.4, 115.6, 44.3, 34.7, 27.1, 26.4. IR (ATR): 3397, 3386, 3324, 3311, 3212, 3026, 2920, 2846, 1604, 1495, 1445, 1265, 1178, 1138, 1000, 807, 692, 515, 474 cm^{-1}. Anal. Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.42; N, 5.57. Found: C, 86.00; H, 8.47; N, 5.58.

*[2]Rotaxane with Pyrrole Moiety (**3a**) (Procedure A).* A mixture of [2]rotaxane (**1**) (25 mg, 0.010 mmol, 1.0 equiv), CuCl (1.0 mg, 0.010 mmol, 1.0 equiv), and aniline **2a** (20 μL, 0.2 mmol, 20 equiv) under Ar atmosphere was stirred at 120 °C for 7 h. The reaction was monitored by TLC using hexane/CH_2Cl_2 (2/1 (v/v)). To the mixture were added CH_2Cl_2 (1.5 mL), CH_3CN (3.5 mL), and aqueous ammonia (30% solution, 1.7 mL). After being stirred at room temperature for 4 h, the mixture was extracted with CH_2Cl_2, and the combined organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by flash silica gel column chromatography using hexane/CH_2Cl_2 (5/3 → 1/1 (v/v)) and GPC using $CHCl_3$ to afford **3a** (19.5 mg, 0.0076 mmol, 76%) as a pale yellow amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.37 (d, *J* = 8.6 Hz, 4H), 8.21 (d, *J* = 8.6 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.72 (s, 2H), 7.55−7.16 (br m, 48H), 7.09−6.99 (m, 6H), 6.91 (d, *J* = 8.0 Hz, 8H), 6.84−6.57 (br m, 4H), 6.42 (s, 1H), 6.40 (s, 2H), 6.29 (s, 2H), 3.78 (t, *J* = 5.7 Hz, 12H), 2.51 (s, 10H), 1.94−1.64 (m, 42H), 1.49−1.08 (m, 50H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 160.53, 160.51, 157.9, 156.5, 147.2, 146.5, 146.3, 139.3 138.5, 138.4, 136.8, 135.4, 132.2, 130.2, 130.0, 129.7, 129.1, 128.8, 127.6, 127.3, 127.2, 127.0, 126.4, 126.1, 125.7, 119.4, 114.9, 114.1, 109.1, 106.9, 101.4, 68.1, 68.0, 67.8, 67.7, 56.1, 44.4, 40.6, 34.7, 34.6, 29.9, 29.8, 29.4, 27.12, 27.05, 26.4, 26.2, 26.0. IR (ATR) 3026, 2920, 2848, 1601, 1587, 1495, 1447, 1243, 1173, 1151, 1004, 833, 811, 773, 525 cm^{-1}. HR-MS (MALDI-TOF) calcd for $C_{186}H_{195}N_3O_6$ ([M + H]$^{+}$): 2567.5119, found 2567.5177.

*[2]Rotaxane with Pyrrole Moiety (**3b**).* Procedure A was generally followed to synthesize **3b** from **2b** (35 mg, 0.20 mmol, 20 equiv), CuCl (1.0 mg, 0.010 mmol, 1.0 equiv), and **1** (25 mg, 0.010 mmol, 1.0 equiv). The crude product was purified by flash silica gel column chromatography using hexane/CH_2Cl_2 (5/3 → 1/1 (v/v)) and GPC using $CHCl_3$ to afford **3b** (19.6 mg, 0.0073 mmol, 74%) as a pale yellow amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.37 (d, *J* = 8.6 Hz, 4H), 8.20 (d, *J* = 8.6 Hz, 2H), 8.01 (d, *J* = 8.6 Hz, 2H), 7.72 (s, 2H), 7.50 (dd, *J* = 8.9, 4.4 Hz, 12H), 7.43 (d, *J* = 8.0 Hz, 6H), 7.39 (d, *J* = 8.0 Hz, 6H), 7.35 (d, *J* = 8.0 Hz, 6H), 7.27−7.18 (m, 19H), 7.07 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 9.2 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 4H), 6.88 (dd, *J* = 8.9, 4.4 Hz, 4H), 6.83 (d, *J* = 7.4 Hz, 4H), 6.61 (d, *J* = 9.2 Hz, 2H), 6.45−6.44 (m, 1H), 6.42 (dd, *J* = 8.3, 2.0 Hz, 2H), 6.30−6.29 (m, 2H), 3.88−3.72 (m, 11H), 2.65−2.44 (m, 10H), 2.24 (t, 1H), 1.91−1.58 (m, 47H), 1.48−1.09 (m, 55H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 160.53, 160.50, 157.9, 157.6, 156.5, 147.3, 147.1, 146.5, 146.4, 146.3, 138.6, 138.40, 138.37, 136.8, 136.7, 135.4, 135.3, 132.2, 130.1, 130.0, 129.8, 129.7, 129.0, 128.7, 127.6, 127.4, 127.3, 127.1,

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127.02, 126.95, 126.5, 126.4, 126.2, 126.1, 125.7, 119.3, 114.9, 114.3, 113.9, 109.0, 108.9, 107.0, 101.4, 68.0, 67.9, 67.8, 56.2, 56.1, 44.4, 43.9, 40.6, 34.7, 34.3, 30.7, 30.4, 30.0, 29.7, 29.5, 29.4, 27.1, 26.9, 26.5, 26.4, 26.21, 26.16, 26.0, 25.9. IR (ATR): 3032, 2921, 2849, 1602, 1587, 1495, 1471, 1446, 1245, 1173, 1004, 811, 527 cm^{-1}. HR-MS (MALDI-TOF) calcd for $C_{192}H_{205}N_3O_6$ ($[M + H]^+$): 2649.5901, found 2649.5892.

*[2]Rotaxane with Pyrrole Moiety (**3c**).* Procedure A was generally followed to synthesize **3c** from **2c** (50 mg, 0.20 mmol, 20 equiv), CuCl (1.0 mg, 0.010 mmol, 1.0 equiv), and **1** (25 mg, 0.010 mmol, 1.0 equiv). The crude product was purified by flash silica gel column chromatography using hexane/CH_2Cl_2 (5/3 → 1/1 (v/v)) and GPC using $CHCl_3$ to afford **3b** (19.4 mg, 0.0071 mmol, 71%) as pale yellow amorphous solid. ^1H NMR (500 MHz, $CDCl_3$) δ: 8.35 (d, J = 8.6 Hz, 4H), 8.19 (d, J = 8.0 Hz, 2H), 7.98 (d, J = 8.0 Hz, 2H), 7.72 (s, 2H), 7.50 (dd, J = 10.9, 8.6 Hz, 12H), 7.43 (d, J = 8.6 Hz, 6H), 7.39 (d, J = 8.6 Hz, 6H), 7.35 (d, J = 8.6 Hz, 6H), 7.30 (dd, J = 10.6, 8.3 Hz, 4H), 7.25 (d, J = 5.2 Hz, 8H), 7.23 (d, J = 8.6 Hz, 6H), 7.20 (d, J = 8.0 Hz, 6H), 7.10−7.04 (m, 5H), 6.94 (d, J = 8.0 Hz, 2H), 6.90 (t, J = 9.7 Hz, 6H), 6.84 (d, J = 9.2 Hz, 2H), 6.62 (d, J = 9.2 Hz, 2H), 6.42 (s, 1H), 6.40 (dd, J = 5.2, 2.6 Hz, 2H), 6.30 (q, J = 3.4 Hz, 2H), 3.85−3.74 (m, 12H), 2.62−2.60 (m, 2H), 2.53−2.51 (m, 9H), 1.82−1.65 (m, 47H), 1.34−1.24 (m, 55H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 160.52, 160.48, 158.0, 157.7, 156.5, 147.5, 147.2, 147.1, 146.5, 146.4, 146.3, 139.5, 138.6, 138.41, 138.38, 138.1, 137.3, 136.8, 135.4, 135.3, 132.2, 130.3, 130.1, 130.0, 129.8, 129.7, 129.3, 129.1, 127.6, 127.4, 127.28, 127.26, 127.03, 127.0, 126.9, 126.5, 126.4, 126.1, 126.0, 125.7, 119.4, 114.9, 114.4, 114.0, 109.3, 109.1, 106.9, 101.5, 68.1, 67.9, 67.8, 56.2, 56.1, 44.4, 34.7, 34.6, 32.1, 30.7, 30.4, 29.9, 29.7, 29.5, 29.3, 27.1, 26.5, 26.4, 26.2, 26.1, 26.0, 22.9, 14.3. IR (ATR): 3026, 2921, 2849, 1602, 1587, 1495, 1446, 1245, 1173, 1151, 1004, 811, 525 cm^{-1}. HR-MS (MALDI-TOF) calcd for $C_{198}H_{209}N_3O_6$ ($[M + H]^+$): 2725.6214, found 2725.6410.

*[2]Rotaxane with Pyrrole Moiety (**3d**).* Procedure A was generally followed to synthesize **3d** from **2d** (60 μL, 0.48 mmol, 20 equiv), CuCl (3.0 mg, 0.024 mmol, 1.0 equiv), and **1** (60 mg, 0.024 mmol, 1.0 equiv). The reaction mixture was stirred at 120 °C for 120 h. The crude product was purified by flash silica gel column chromatography using hexane/CH_2Cl_2 (5/3 → 1/1 (v/v)) and GPC using $CHCl_3$ to afford **3b** (26 mg, 0.010 mmol, 42%) as a pale yellow amorphous solid. ^1H NMR (500 MHz, $CDCl_3$) δ: 8.38 (d, J = 8.6 Hz, 4H), 8.20 (d, J = 8.6 Hz, 2H), 8.00 (d, J = 8.6 Hz, 2H), 7.71 (s, 2H), 7.46−7.44 (brm, 24H), 7.31−7.29 (brm, 12H), 7.23−7.21 (brm, 17H), 7.09 (t, J = 8.0 Hz, 1H), 6.92 (d, J = 9.2 Hz, 8H), 6.52 (t, J = 10.0 Hz, 1H), 6.44 (dd, J = 8.0, 2.3 Hz, 2H), 6.06 (s, 2H), 3.91 (t, J = 10.0 Hz, 4H), 3.85−3.80 (m, 10H), 2.50 (s, 10H), 1.89−1.73 (m, 45H), 1.46−1.16 (m, 55H), 1.00−0.99 (m, 2H), 0.66−0.63 (m, 2H), 0.38 (t, J = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 160.6, 160.5, 158.3, 156.5, 147.2, 146.5, 146.3, 138.5, 138.4, 136.9, 135.8, 132.2, 130.4, 130.0, 129.7, 129.1, 127.7, 127.4, 127.0, 126.9, 126.4, 125.8, 119.4, 114.8, 114.6, 108.7, 106.9, 101.5, 68.2, 68.1, 67.8, 56.1, 44.4, 40.6, 34.7, 32.9, 30.6, 29.8, 29.4, 27.1, 26.4, 26.2, 26.0, 19.5, 13.6. IR (ATR): 3083, 3028, 2922, 2849, 1601, 1587, 1494, 1420, 1245, 1173, 1151, 1004, 833, 810, 527 cm^{-1}. HR-MS (MALDI-TOF) calcd for $C_{184}H_{199}N_3O_6$ ($[M + H]^+$): 2547.5432, found 2547.5488.

*[2]Rotaxane−CuCl Complex (**4**).* To a solution of [2]rotaxane (**1**) (82 mg, 0.03 mmol, 1.0 equiv) in CH_2Cl_2 (1.4 mL) was added a solution of CuCl (33 mg, 0.03 mmol, 1.0 equiv) in CH_3CN (0.6 mL) was stirred at room temperature for 24 h, and the reaction mixture was concentrated in vacuo. The crude product was purified by flash silica gel column chromatography using hexane/CH_2Cl_2 (1/1 → 1/5 (v/v)) to afford **4** (48 mg, 0.02 mmol, 65%) as an orange amorphous solid. ^1H NMR (500 MHz, $CDCl_3$) δ: 8.30 (d, J = 8.6 Hz, 4H), 8.26 (brs, 2H), 7.97−7.95 (brm, 2H), 7.78 (s, 2H), 7.49 (dd, J = 8.3, 4.2 Hz, 24H), 7.35 (d, J = 8.6 Hz, 12H), 7.25 (d, J = 8.0 Hz, 12H), 7.20−7.14 (m, 4H), 7.09 (t, J = 8.3 Hz, 1H), 6.86 (d, J = 8.0 Hz, 4H), 6.72 (d, J = 7.4 Hz, 4H), 6.63 (s, 1H), 6.45 (dd, J = 8.0, 1.7 Hz, 2H), 3.88 (t, J = 6.3 Hz, 4H), 3.84−3.82 (brm, 4H), 3.78 (t, J = 6.9 Hz, 4H), 2.64−2.57 (m, 4H), 2.56−2.47 (m, 6H), 1.94−1.61 (m, 42H), 1.48−1.17 (m, 52H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 160.6, 160.5, 159.8, 158.6, 147.2, 146.5, 143.9, 138.6, 138.3, 137.5, 134.0, 131.5, 131.1, 129.9, 129.8, 129.3, 127.5, 127.4, 127.0, 126.4, 125.9, 124.2, 114.7, 114.4, 107.4, 101.0, 85.7, 74.7, 68.3, 68.0, 67.8, 56.2, 44.4, 40.6, 34.6, 30.4, 29.6, 29.4, 29.0, 27.1, 26.4, 26.2, 25.9, 25.6. IR (ATR): 3024, 2921, 2849, 1600, 1585, 1494, 1470, 1247, 1169, 1151, 1004, 830, 811, 530, 403 cm^{-1}. Anal. Calcd for $C_{180}H_{188}ClCuN_2O_6$: C, 83.98; H, 7.36; N, 1.09. Found: C, 83.65; H, 7.36; N, 1.20.

*Axle Component with Pyrrole Moiety (**6**) (Procedure B).* A mixture of 1,3-diyne (**5**) (18 mg, 0.010 mmol, 1.0 equiv), CuCl (1.0 mg, 0.010 mmol, 1.0 equiv), and aniline (**2a**) (20 μL, 0.20 mmol, 20 equiv) was stirred at 120 °C for 7 h. The reaction was monitored by TLC using hexane/CH_2Cl_2 (5/1 (v/v)). The reaction mixture was cooled to room temperature and concentrated in vacuo. The crude product was purified by flash silica gel column chromatography using hexane/CH_2Cl_2 (6/1 (v/v)) and GPC using $CHCl_3$ to afford **6** (15 mg, 0.0078 mmol, 78%) as a pale yellow amorphous solid. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.50 (dd, J = 8.6, 4.3 Hz, 24H), 7.36 (d, J = 8.6 Hz, 12H), 7.25 (d, J = 9.2 Hz, 12H), 7.18 (t, J = 3.2 Hz, 2H), 6.99−6.96 (m, 1H), 6.93 (d, J = 8.6 Hz, 4H), 6.66 (d, J = 8.6 Hz, 4H), 6.36 (s, 2H), 3.83 (t, J = 6.3 Hz, 4H), 2.56 (dd, J = 36.7, 25.2 Hz, 10H), 1.94−1.63 (m, 33H), 1.50−1.14 (m, 45H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 157.8, 147.3, 146.5, 139.3, 138.7, 138.4, 135.4, 130.1, 129.8, 129.2, 128.9, 127.4, 127.2, 127.0, 126.5, 126.0, 114.1, 109.1, 68.0, 56.2, 44.4, 40.7, 34.7, 30.4, 29.5, 27.1, 26.4, 26.1, 25.9. IR (ATR): 3025, 2920, 2848, 1608, 1496, 1467, 1446, 1385, 1240, 1174, 1004, 773, 529 cm^{-1}. HR-MS (ESI) calcd for $C_{144}H_{153}NO_2$ ($[M]^+$): 1928.1891, found 1928.1896.

*Axle Component with Pyrrole Moiety (**9**).* Procedure B was generally followed to synthesize **9**. A mixture of **2b** (70 mg, 0.40 mmol, 20 equiv), CuCl (1.0 mg, 0.010 mmol, 1.0 equiv), and **5** (36 mg, 0.020 mmol, 1.0 equiv) was stirred at 120 °C for 24 h. The crude product was purified by flash silica gel column chromatography using hexane/CH_2Cl_2 (5/3 → 1/1 (v/v)) and GPC using $CHCl_3$ to afford **9** (22 mg, 0.011 mmol, 55%) as a pale yellow amorphous solid. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.51 (dd, J = 8.9, 4.4 Hz, 24H), 7.37 (d, J = 8.0 Hz, 12H), 7.25 (t, J = 6.6 Hz, 12H), 7.02 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.6 Hz, 4H), 6.89 (d, J = 8.6 Hz, 2H), 6.65 (d, J = 8.6 Hz, 4H), 6.36 (s, 2H), 3.84 (t, J = 6.3 Hz, 4H), 2.67−2.60 (m, 4H), 2.57−2.50 (m, 6H), 2.47−2.40 (m, 1H), 1.94−1.65 (m, 39H), 1.50−1.16 (m, 51H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 157.7, 147.3, 146.5, 138.7, 138.4, 135.4, 130.0, 129.8, 128.8, 127.4, 127.2, 127.0, 126.5, 126.1, 114.0, 108.9, 68.0, 56.2, 44.4, 44.2, 40.7, 34.7, 34.6, 30.4, 29.5, 27.1, 27.0, 26.4, 26.3, 26.2, 25.9. IR (ATR) 3025, 2920, 2848, 2657, 1903, 1608, 1513, 1496, 1446, 1385, 1240, 1174, 1004, 830, 810, 777, 527 cm^{-1}. HR-MS (ESI) calcd for $C_{150}H_{163}NO_2$ ($[M]^+$): 2010.2678, found 2010.2700. Anal. Calcd for $C_{150}H_{163}NO_2 \cdot H_2O$: C, 88.75; H, 8.19; N, 0.69. Found: C, 88.84; H, 8.22; N, 0.74.

*Phenanthroline−CuCl Complex (**7**) (Procedure C).* A reported procedure[5a] was generally followed to synthesize **7**. To a solution of 2,9-bis(4-methoxyphenyl)-1,10-phenanthroline (**13**, 157 mg, 0.40 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) was added the solution of CuCl (40 mg, 0.40 mmol, 1.0 equiv) in CH_3CN (8 mL). After 1 h of stirring, the solvent was removed in vacuo. The residue was purified by recrystallization from hexane−CH_2Cl_2 to afford **7** (168 mg, 0.34 mmol, 85%) as a purple powder. Mp: 233.2−233.9 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 8.48 (d, J = 8.6 Hz, 2H), 8.00 (s, 2H), 7.84 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.6 Hz, 4H), 6.03 (d, J = 8.6 Hz, 4H), 3.46 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 160.3, 156.6, 143.7, 137.3, 131.3, 129.4, 128.0, 126.3, 124.7, 112.8, 55.5. IR (ATR): 3046, 3007, 2955, 2933, 2906, 2832, 1606, 1583, 1496, 1488, 11254, 1176, 1026, 830 cm^{-1}. Anal. Calcd for $C_{26}H_{20}ClCuN_2O_2 \cdot H_2O$: C, 61.30; H, 4.35; N, 5.50. Found: C, 61.02; H, 4.17; N, 5.44.

*Macrocyclic Phenanthroline−CuCl Complex (**8**).* Procedure C was generally followed to synthesize **8**. To a solution of a macrocyclic phenanthroline (**14**, 144 mg, 0.23 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added the solution of CuCl (22.3 mg, 0.23 mmol, 1.0 equiv) in CH_3CN (4 mL). After 1 h of stirring, the solvent was removed in vacuo. The residue was purified by recrystallization from hexane−CH_2Cl_2 to afford **8** (116 mg, 0.16 mmol, 70%) as a pale brown powder. Mp: 118.4−119.1 °C. ^1H NMR (500 MHz, $CDCl_3$) δ: 8.73−

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7.61 (m, 10H), 7.13 (t, J = 8.0 Hz, 1H), 7.03 (s, 4H), 6.57 (s, 1H), 6.47 (dd, J = 8.0, 2.3 Hz, 2H), 4.01 (t, J = 7.2 Hz, 4H), 3.94 (t, J = 6.0 Hz, 4H), 1.93−1.38 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 161.4, 160.7, 137.8, 129.8, 126.3, 114.8, 107.0, 101.3, 68.0, 29.8, 28.9, 26.0 (some signals are missing). IR (ATR): 3060, 3038, 2937, 2863, 1604, 1586, 1489, 1253, 1177, 1152, 1019, 836 cm^{-1}. HR-MS (ESI) calcd for $C_{42}H_{42}N_2O_4ClCu$ ([M]$^+$): 736.2125, found 736.2124.

Synthesis of 11. *4,4,4-Tris(4′-cyclohexyl[1,1′-biphenyl]-4-ylbutan-1-ol (17).* A reported procedure[5a] was generally followed to synthesize **17**. To a solution of tris(4′-cyclohexyl[1,1′-biphenyl]-4-yl)methane (**15**, 0.50 g, 0.70 mmol, 1.0 equiv) in dry THF (3 mL) was added 1.6 M *n*-BuLi in hexane (0.85 mL, 1.4 mmol, 2.0 equiv) with stirring at room temperature under Ar. To the resulting blue suspension was added 1-bromo-3-(methoxymethoxy)propane (**16**, 0.13 g, 0.70 mmol, 1.0 equiv) at room temperature. After 24 h, the reaction mixture was diluted with MeOH (6.1 mL), and concd HCl (0.6 mL) was added. The mixture was then heated to 60 °C and stirred for overnight. After the addition of water, the mixture was extracted with CH_2Cl_2. The combined organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate = 10/1) as the eluent to afford **17** (0.54 g, 0.45 mmol, 65%) as a white amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.51 (dd, J = 7.7, 4.9 Hz, 12H), 7.39 (d, J = 8.0 Hz, 6H), 7.26 (d, J = 8.6 Hz, 6H), 3.66 (t, J = 6.6 Hz, 2H), 2.73−2.72 (m, 2H), 2.54−2.52 (m, 3H), 1.94−1.71 (m, 15H), 1.53−1.20 (m, 17H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 147.3, 146.2, 138.8, 138.4, 129.8, 127.4, 127.0, 126.6, 63.6, 55.9, 44.4, 36.71, 34.66, 29.4, 27.1, 26.4. IR (ATR): 3582, 3437, 3025, 2921, 2848, 2662, 1905, 1495, 1446, 1004, 809, 779, 527 cm^{-1}. HR-MS (ESI) calcd for $C_{58}H_{64}ONa$ ([M + Na]$^+$): 799.4849, found 799.4881. Anal. Calcd for $C_{58}H_{64}O·H_2O$: C, 87.61; H, 8.37. Found: C, 87.75; H, 8.41.

4,4,4-Tris(4′-cyclohexyl[1,1′-biphenyl]-4-yl)-1-(4-ethynyltrimethylsilylphenoxy)butane (19). A reported procedure[21] was generally followed to synthesize **19**. To a solution of 2-(4-hydroxyphenyl)-1-trimethylsilylacetylene (**18**) (73.4 mg, 0.32 mmol, 1.2 equiv) and PPh_3 (100 mg, 0.38 mmol, 1.2 equiv) in dry THF (1 mL) was added to a solution of 4,4,4-tris(4′-cyclohexyl-[1,1′-biphenyl]-4-yl)butan-1-ol (**17**) (250 mg, 0.32 mmol, 1.0 equiv) and diethyl azodicarboxylate (40% toluene solution, 0.17 mL, 0.38 mmol, 1.2 equiv) in dry THF (1 mL), and the solution was refluxed under Ar atmosphere for 23 h. The solvent was removed in vacuo, and the residue was purified by short flash silica gel column chromatography using hexane/CH_2Cl_2 (10/1 (v/v)) to afford **19** (252 mg, 0.27 mmol, 83%) as a white amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.51 (dd, J = 4.9, 3.1 Hz, 12H), 7.40 (dd, J = 8.6, 5.2 Hz, 8H), 7.27 (d, J = 8.0 Hz, 6H), 6.81 (d, J = 8.6 Hz, 2H), 3.94 (t, J = 6.0 Hz, 2H), 2.86−2.80 (m, 0H), 2.57−2.49 (m, 3H), 1.95−1.64 (m, 18H), 1.50−1.21 (m, 16H), 0.25 (d, J = 3.4 Hz, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.4, 147.3, 146.1, 138.9, 138.4, 133.7, 129.8, 127.4, 127.1, 126.6, 115.3, 114.6, 105.5, 92.6, 68.3, 55.9, 44.4, 36.9, 27.1, 26.4, 26.0. IR (ATR): 3026, 2922, 2849, 2152, 1604, 1504, 1447, 1245, 1003, 863, 838, 811, 538 cm^{-1}. HR-MS (ESI) calcd for $C_{69}H_{76}OSi$ ([M]$^+$): 948.5674, found 948.5660.

4,4,4-Tris(4′-cyclohexyl[1,1′-biphenyl]-4-yl)-1-(4-ethynylphenoxy)butane (20). A reported procedure[21] was generally followed to synthesize **20**. A mixture of **19** (180 mg, 0.19 mmol, 1.0 equiv) and K_2CO_3 (131 mg, 0.95 mmol, 5.0 equiv) in MeOH (2 mL) and THF (1 mL) was stirred at room temperature for 24 h. The solvent was removed in vacuo. To the mixture was added water and CH_2Cl_2. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by short flash silica gel column chromatography using hexane/CH_2Cl_2 (8/1 (v/v)) to afford **20** (150 mg, 0.17 mmol, 90%) as a white amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.54 (dd, J = 8.0, 4.6 Hz, 12H), 7.43 (dd, J = 4.0, 2.0 Hz, 8H), 7.28 (d, J = 8.0 Hz, 6H), 6.85 (d, J = 8.6 Hz, 2H), 3.94 (t, J = 6.3 Hz, 2H), 3.01 (s, 1H), 2.85−2.85 (m, 2H), 2.60−2.51 (m, 3H), 1.98−1.66 (m, 15H), 1.53−1.23 (m, 17H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 159.6, 147.3, 146.1, 138.8, 138.3, 133.8, 129.7, 127.4, 127.0, 126.6, 114.7, 114.2, 84.0, 76.0, 68.3, 55.9, 44.4, 36.8, 34.6, 27.1, 26.4, 26.0. IR (ATR) 3313, 3286, 3025, 2848, 1605, 1503, 1495, 1446, 1245, 1004, 809, 533 cm^{-1}. HR-MS (ESI) calcd for $C_{66}H_{69}O$ ([M + H]$^+$): 877.5343, found 877.5335. Anal. Calcd for $C_{66}H_{68}O·H_2O$: C, 88.54; H, 7.88. Found: C, 88.25; H, 7.71.

[2]Rotaxane (11). A reported procedure[21] was generally followed to synthesize **11**. A mixture of **20** (44 mg, 0.050 mmol, 2.5 equiv), macrocyclic phenanthroline−CuI complex (**21**) (17 mg, 0.02 mmol, 1.0 equiv), K_2CO_3 (10 mg, 0.075 mmol, 3.8 equiv), and I_2 (6.3 mg, 0.025 mmol, 1.3 equiv) in dry xylene (1.0 mL) under Ar atmosphere was stirred at 130 °C for 20 h. The solution was cooled to room temperature, and CH_2Cl_2 (1.5 mL), CH_3CN (3.5 mL) and aqueous ammonia (30% solution, 1.7 mL) were added. After being stirred at room temperature for 4 h, the solution was extracted with CH_2Cl_2, and the combined organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash silica gel column chromatography using hexane/CH_2Cl_2 (3/1 (v/v)) and GPC using $CHCl_3$ to afford **11** (29 mg, 0.014 mmol, 70%) as a colorless amorphous solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.39 (d, J = 8.6 Hz, 4H), 8.19 (d, J = 8.6 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H), 7.69 (s, 2H), 7.47 (d, J = 8.0 Hz, 16H), 7.43 (d, J = 8.6 Hz, 12H), 7.27 (d, J = 8.0 Hz, 12H), 7.24 (d, J = 8.6 Hz, 14H), 7.13 (t, J = 8.0 Hz, 1H), 6.96 (d, J = 9.2 Hz, 4H), 6.82 (d, J = 8.6 Hz, 4H), 6.68 (s, 1H), 6.48 (dd, J = 8.0, 2.3 Hz, 2H), 3.97 (t, J = 6.6 Hz, 4H), 3.91 (t, J = 7.2 Hz, 4H), 3.82 (t, J = 6.0 Hz, 4H), 2.65−2.60 (m, 4H), 2.55−2.48 (m, 6H), 1.93−1.72 (m, 38H), 1.55−1.21 (m, 42H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 160.7, 160.5, 160.0, 156.7, 147.3, 146.3, 146.0, 138.7, 138.3, 136.8, 134.3, 132.2, 129.9, 129.7, 129.2, 127.6, 127.4, 127.0, 126.5, 125.8, 119.5, 114.98, 114.96, 113.8, 107.4, 100.9, 81.8, 73.7, 68.5, 68.1, 68.0, 55.8, 44.4, 36.7, 34.7, 29.8, 29.3, 27.1, 26.4, 26.1, 26.0, 25.9. IR (ATR): 3026, 2921, 2848, 1905, 1600, 1587, 1493, 1471, 1446, 1285, 1245, 1169, 1151, 1018, 1004, 905, 831, 810, 797, 729, 687, 639, 629, 563, 530, 511 cm^{-1}. HR-MS (MALDI-TOF) calcd for $C_{174}H_{176}N_2O_6$ ([M + H]$^+$): 2390.3601, found 2390.3626.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02911.

Spectral data for new compounds, and the details of VT NMR studies (PDF)

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Notes

The authors declare no competing financial interest.

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