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Using Diels–Alder reactions to synthesize [2]rotaxanes under solvent-free conditions

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ABSTRACT

Diels–Alder reactions of the terminal alkyne units of SiO_2-supported [2]pseudorotaxanes with 1,2,4,5-tetrazine derivatives proceed efficiently through solid-to-solid contact to provide both asymmetric and symmetric [2]rotaxanes incorporating either 24- or 25-membered-ring macrocycles.

1. Introduction

Several [2]rotaxanes, supermolecular compounds comprising an interlocked macrocycle and a dumbbell-shaped thread component, have been developed as components for molecular electronic devices.[1] Among the protocols that can be used to synthesize rotaxanes, the 'threading-followed-by-stoppering' approach[2] is one of the most straightforward; it relies on weak intermolecular interactions to position the threadlike component within the cavity of the macrocycle and then the interlocking of the components of the resulting pseudorotaxane is performed using a suitable stoppering reaction. The formation of pseudorotaxanes from crown ethers and dibenzylammonium (DBA) ions in solution has been studied now for almost 15 years; the application of this binding motif has resulted in many elegant interlocked molecules and functional materials.[3] The efficiency of rotaxane syntheses from their pseudorotaxane precursors in solution is, however, frequently affected by factors such as the concentration of the mixture, competing solvents, and the formation of interfering byproducts. Because these disturbing influences are less pronounced in the solid state, reactions that can proceed under solvent-free conditions would be ideal for the efficient synthesis of crown ether/DBA ion-based rotaxanes. Because of the paucity of known stoppering reactions that proceed efficiently under the conditions of direct solid-to-solid contact, only a few such syntheses have been reported so far.[4] Previously, we revealed that the ball-milling of terminal alkynes and 1,2,4,5-tetrazine produces pyridazine rings, which are sufficiently sterically bulky to interlock the small [21]crown-7 (21C7)[5] macrocycle; using this approach, we synthesized what we believe is the smallest [2]rotaxane ever prepared.[6] To apply this synthetic method to the construction of functional interlocked molecules, it was necessary for us to broaden the reaction's scope so that we could interlock macrocycles more sizable than 21C7. Herein, we report a modified set of reaction conditions for this solvent-free stoppering approach, one that allows the efficient interlocking of 24- and 25-membered-ring macrocycles in the form of [2]rotaxanes.

2. Results and discussion

Previously, we demonstrated that Diels–Alder reactions between terminal alkynes and 1,2,4,5-tetrazine proceed efficiently under solid-to-solid ball-milling conditions.[6]

Based on the knowledge that macrocycle **1** can complex DBA ions tightly in low-polarity solvents,[7] for its use as the threadlike component we synthesized the salt **2**-H·PF_6, which contains a *p*-*tert*-butyl phenyl terminus (i.e., a stopper for **1**) and a terminal alkyne unit, from the amine **3** and the aldehyde **4** through sequential condensation, reduction, and ion exchange processes (Scheme 1). We calculated the association constants for the interactions between macrocycle **1** and thread **2**-H·PF_6 in CD_3CN and CD_3NO_2 to be 350 and 8600 M^{-1}, respectively, based on a ^{1}H NMR spectroscopy-based single-point method.[8] Thus, we expected that concentrating an equimolar solution of the macrocycle **1** and the threadlike salt **2**-H·PF_6 would result in a solid containing predominantly the [2]pseudorotaxane complex [(**1**⊃**2**-H)·PF_6].[9]

Concentrating an equimolar mixture of the macrocycle **1** and the threadlike salt **2**-H·PF_6 in CH_3NO_2 provided a sticky liquid rather than a solid; therefore, we added silica gel to the solution and then evaporated the organic solvent under reduced pressure. Because macrocycle **1** forms a [2]pseudorotaxane with DBA in low-polarity solvents, and because unsubstituted pyridazine rings are

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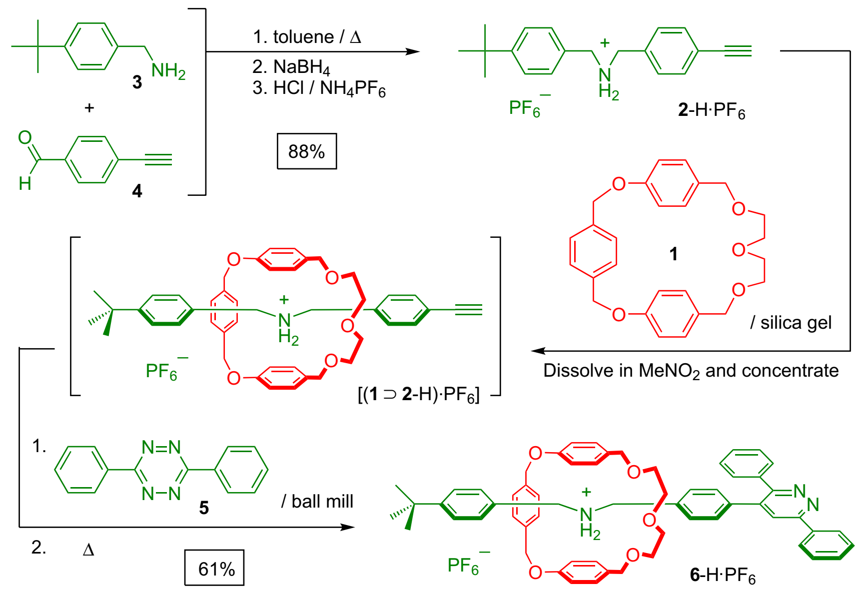


Scheme 1.

smaller than a benzene ring, we suspected that the pyridazine unit generated from the reaction of a terminal alkyne with 1,2,4,5-tetrazine would not be a true stopper for interlocking the macrocycle **1** within a [2]rotaxane. Thus, we applied 3,6-diphenyl-1,2,4,5-tetrazine (**5**) to the reaction with the expectation that the steric bulk of the resulting diphenylpyridazine would be sufficient to prevent dethreading of macrocycle **1** from the resulting [2]rotaxane. From ^{1}H NMR spectroscopic analyses, the ball-milling of an equimolar mixture of the SiO_2-supported [2]pseudorotaxane [(**1**⊃**2**-H)·PF_6] and the solid diphenyltetrazine **5** for up to 12 h produced no detectable signals for the desired [2]rotaxane. Because the grinding of 1,2,4,5-tetrazine with the same SiO_2-supported [2]pseudorotaxane [(**1**⊃**2**-H)·PF_6] produced a reasonable amount of the corresponding pyridazine-terminated dumbbell component within 9 h under the same ball-milling conditions, it appeared that the problem in our [2]rotaxane synthesis was the relatively low reactivity of 3,6-diphenyl-1,2,4,5-tetrazine. Relative to 1,2,4,5-tetrazine, which sublimed readily at high temperature to afford a low yield of our 'smallest [2]rotaxane' synthesized under thermal conditions,[5] 3,6-diphenyl-1,2,4,5-tetrazine is less volatile; therefore, we suspected that heating a well-ground solid mixture of the SiO_2-supported [2]pseudorotaxane [(**1**⊃**2**-H)·PF_6] and the diphenyltetrazine **5** at high temperature would allow the stoppering reaction to proceed efficiently under the solid-to-solid contact. Thus, we ground the SiO_2-supported [2]pseudorotaxane [(**1**⊃**2**-H)·PF_6] with the diphenyltetrazine **5** for 1 h and then heated the mixture at 373 K under atmosphere pressure.[10] To monitor the progress of the reaction, at various time intervals we dissolved a portion of the solid reaction mixture in CD_3CN, filtered off the SiO_2, and then recorded the ^{1}H NMR spectrum of the filtrate. Over time, we observed a new set of signals appeared with increasing intensity (Fig. 1). After heating at 373 K for 3 days, these signals predominated the spectrum (Fig. 1d); thus, we subjected the mixture to column chromatography (SiO_2: MeOH/CH_2Cl_2, 2:98) and isolated the [2]rotaxane **6**-H·PF_6 in 61% yield. Similar reactions performed in solution did not proceed as efficiently as it did in the solid state; indeed, heating an equimolar (20 mM) mixture of the macrocycle **1**, the threadlike salt **2**-H·PF_6, and the diphenyltetrazine **5** in CD_3CN (at 343 K) or CD_3NO_2 (at 353 K) gave a complicated set of products after 3 days.

To demonstrate that the same synthetic method could be applied to synthesize a symmetric [2]rotaxane, we synthesized the diyne **10**-H·PF_6 in three steps from the amine **7** (Scheme 2). Boc-protection of **7** followed by Sonogashira coupling of the resulting dibromide **8** with trimethylsilylacetylene afforded the diyne **9**. Removal of the silyl and Boc protecting groups of **9** under basic and acidic conditions, respectively, with subsequent ion exchange and column chromatography, gave the desired threadlike salt **10**-H·PF_6. Concentrating a mixture of the macrocycle **1**, the threadlike diyne **10**-H·PF_6, and SiO_2 in CH_3NO_2 gave a solid, which we assumed

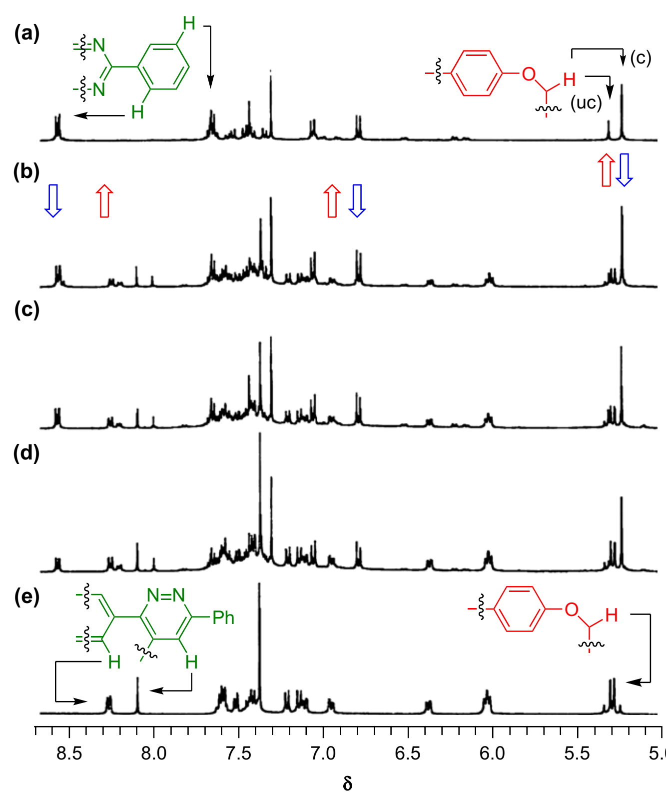
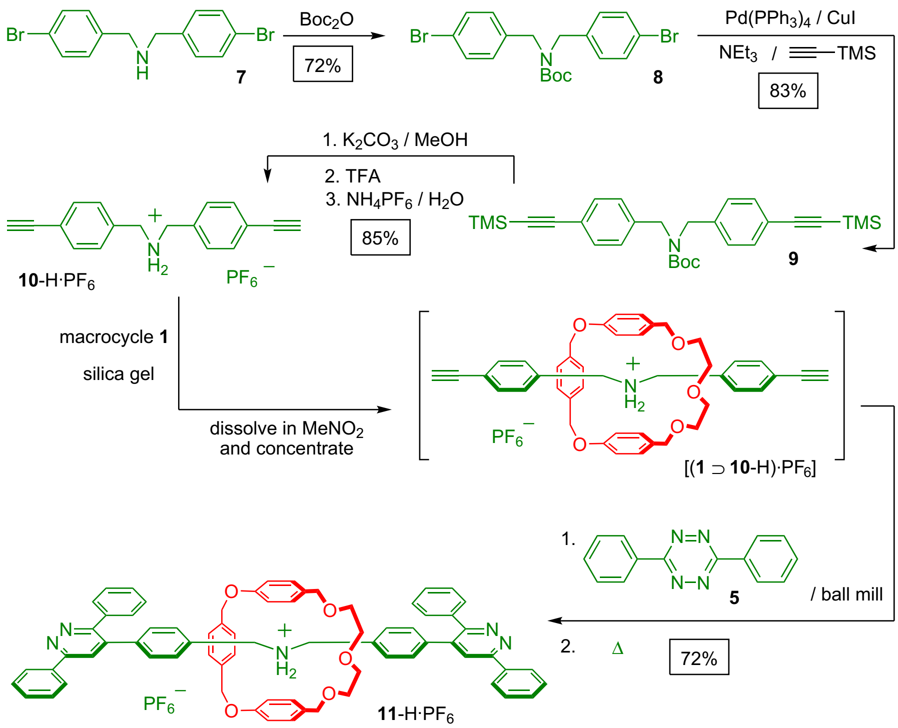


Figure 1. Partial ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) revealing the formation of the [2]rotaxane **6**-H·PF_6 during the heating of a ball-milled (1 h) solid mixture of the SiO_2-supported [2]pseudorotaxane [**1**⊃**2**-H][PF_6] and the diphenlytetrazine **5** for (a) 0, (b) 24, (c) 48, and (d) 72 h; (e) spectrum of isolated **6**-H·PF_6.



Scheme 2.

contained predominantly the [2]pseudorotaxane [(**1**⊃**10**-H)·PF_6]. Ball-milling of this solid in the presence of the diphenyltetrazine **5** (molar ratio, 1:2) for 1 h and then heating the resulting solid mixture at 373 K for 3 days gave the desired symmetrical [2]rotaxane **11**-H·PF_6, which we isolated in 72% yield after column chromatography (SiO_2: MeOH/CH_2Cl_2, 2:98). Relative to the ^{1}H NMR spectra of **1** and **10**-H·PF_6 (Fig. 2), the significant upfield shift for the signal of the methylene proton adjacent to the NH_2^+ center in the [2]rotaxane **11**-H·PF_6 and the separation of the originally overlapping signals (at δ 3.46) for the protons of the ethylene glycol unit into separate signals at δ 3.09 and 3.52, confirmed that [N–H···O] and [C–H···π] hydrogen bonds were important noncovalent interactions stabilizing the recognition of the macrocycle **1** by the dumbbell-shaped salt. Thus, both asymmetric and symmetric [2]rotaxanes featuring the 25-membered-ring macrocycle **1** were efficiently synthesized using the same solvent-free Diels–Alder reaction, i.e., by simply heating a well-ground mixture of the SiO_2-supported alkyne-terminated [2]pseudorotaxanes and 3,6-diphenyl-1,2,4,5-tetrazine at 373 K for a few days.

To prove the generality of this synthetic method, we mixed the threadlike salts **2**-H·PF_6 and **10**-H·PF_6 individually with SiO_2 and dibenzo[24]crown-8 (DB24C8) in solution and concentrated the mixtures to produce the corresponding solids coating with the [2]pseudorotaxanes [(DB24C8⊃**2**-H)·PF_6] and [(DB24C8⊃**10**-H)·PF_6], respectively (Scheme 3). Grinding these solids individually with the diphenyltetrazine **5** for 1 h and then heating the resulting solid mixtures at 373 K for 3 days afforded the desired asymmetric and symmetric [2]rotaxanes **12**-H·PF_6 (73%) and **13**-H·PF_6 (72%), respectively, after column chromatography (SiO_2: MeOH/CH_2Cl_2, 2:98). Figure 3 reveals the gradual formation of the [2]rotaxane

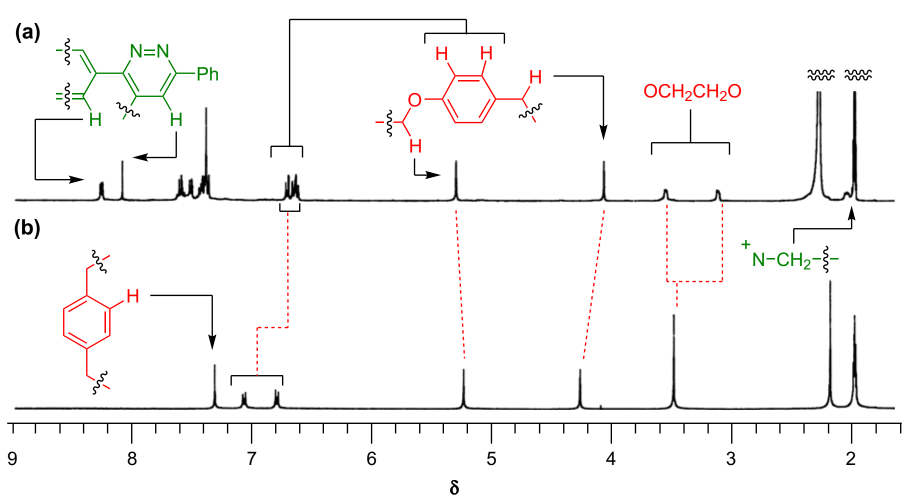
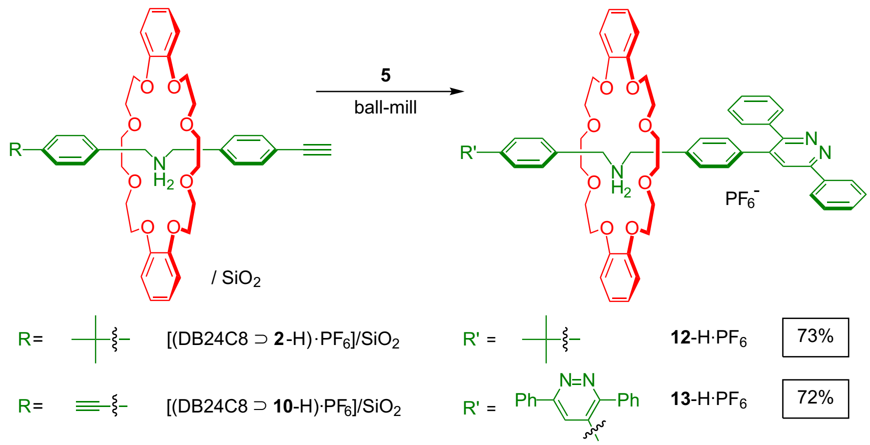


Figure 2. ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of (a) the symmetric [2]rotaxane **11**-H·PF_6 and (b) the macrocycle **1**.



Scheme 3.

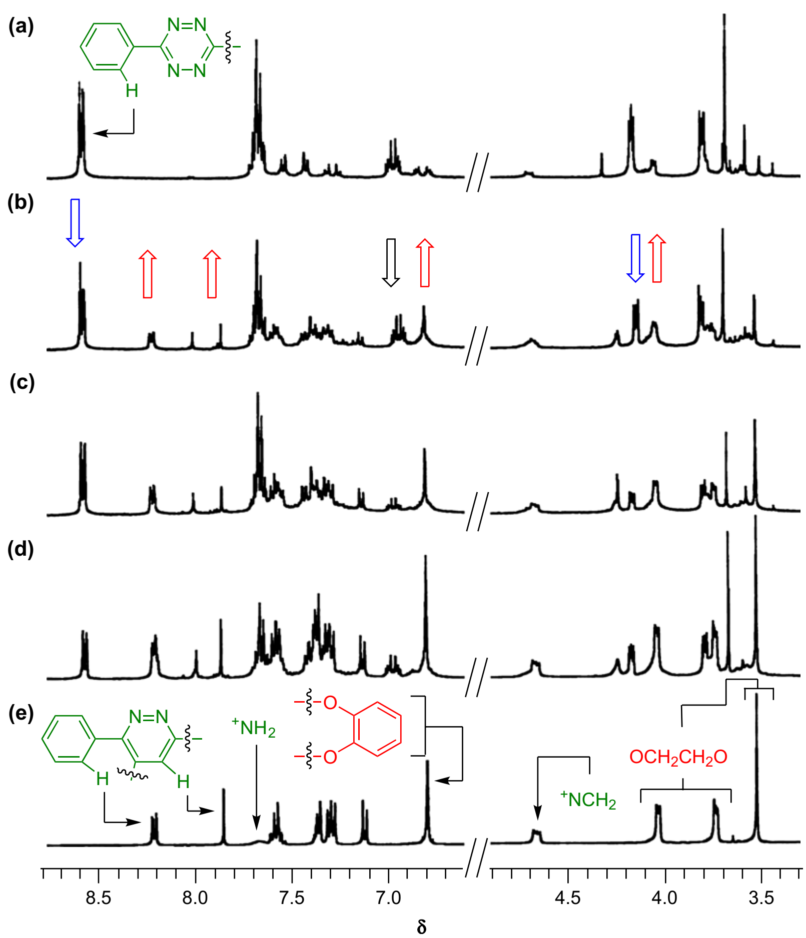


Figure 3. Partial ^1H NMR spectra (400 MHz, CD_3CN, 298 K) displaying the formation of the [2]rotaxane **13**-H·PF_6 during the heating of a ball-milled (1 h) solid mixture of the SiO_2-supported [2]pseudorotaxane [DB24C8⊃**10**-H][PF_6] and the diphenyltetrazine **5** for (a) 0, (b) 24, (c) 48, and (d) 72 h; (e) spectrum of isolated **13**-H·PF_6.

13-H·PF_6 during this 'grinding-followed-by-heating' process. Thus, the efficiency of this stoppering method was retained when changing the nature of the macrocyclic component.

3. Conclusion

We have demonstrated that the Diels–Alder reactions of the terminal alkyne units of SiO_2-supported [2]pseudorotaxanes with 1,2,4,5-tetrazine derivatives proceed efficiently through solid-to-solid contact to provide both asymmetric and symmetric [2]rotaxanes incorporating either of the macrocycles **1** or DB24C8. We suspect that the convenience and environmentally benign nature of this synthetic method will be helpful for the construction of other complex interlocked molecules exhibiting various functions. The presence of the pyridazine termini of these [2]rotaxanes provides the possibility of using them as building blocks for assembling complicated molecular architectures in the presence of suitable metal ions; such studies are under investigation in our laboratory.

4. Experimental

4.1. General

All glassware, stirrer bars, syringes, and needles were either oven- or flame-dried prior to use. All reagents, unless otherwise indicated, were obtained from commercial sources. Anhydrous CH_2Cl_2 and MeCN were obtained through distillation from CaH_2 under N_2. Anhydrous THF was obtained through distillation from Na/Ph_2CO under N_2. Reactions were conducted under N_2 or Ar atmospheres. Thin layer chromatography (TLC) was performed on Merck 0.25-mm silica gel (Merck Art. 5715). Column chromatography was undertaken over Kieselgel 60 (Merck, 70–230 mesh). Melting points are uncorrected. Ball-milling was performed using a Retsch MM 200 swing-mill, containing two 5-mL stainless-steel cells and two stainless-steel balls (diameter: 7 mm); the mill was operated at a frequency of 22.5 Hz at room temperature. In NMR spectra, the deuterated solvent was used as the lock; the role of the internal standard was played by either TMS or the solvent's residual protons. Chemical shifts are reported in parts per million (ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), m (mutiplet), and br (broad).

4.2. [2]Rotaxane 6-H·PF_6

The organic solvent was evaporated under reduced pressure from a mixture of macrocycle **1** (100 mg, 0.24 mmol), the alkyne **2**-H·PF_6 (100 mg, 0.24 mmol), and silica gel (200 mg) in CH_3NO_2 (10 mL) to afford a solid mixture, which was then mixed with 3,6-diphenyl-1,2,4,5-tetrazine (61 mg, 0.26 mmol) and ball-milled at room temperature for 1 h. The solid mixture was transferred to a 5 mL flask, heated to 100 °C for 3 days, and then purified chromatographically (SiO_2: MeOH/CH_2Cl_2, 2:98) to afford the [2]rotaxane **6**-H·PF_6 as a white solid (153 mg, 61%). Mp=173–174 °C; ^{1}H NMR (400 MHz, CD_3CN): δ=1.05 (t, *J*=7 Hz, 2H), 1.41 (s, 9H), 2.99 (t, *J*=6 Hz, 2H), 3.02–3.09 (m, 2H), 3.26–3.31 (m, 2H), 3.55–3.60 (m, 4H), 3.80 (d, *J*=9 Hz, 2H), 4.28 (d, *J*=9 Hz, 2H), 5.27 (dd, *J*=25, 15 Hz, 4H), 5.97–6.02 (m, 4H), 6.35 (dd, *J*=8, 2 Hz, 2H), 6.95 (dd, *J*=9, 3 Hz, 2H), 7.10–7.21 (m, 6H), 7.37 (s, 4H), 7.39–7.54 (m, 7H), 7.55–7.63 (m, 5H), 8.10 (s, 1H), 8.27 (dd, *J*=7, 2 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ=31.5, 35.5, 49.1, 52.5, 68.2, 69.8, 71.3, 74.4, 115.0, 125.6, 126.6, 126.8, 127.2, 127.9, 128.0, 129.0, 129.2, 129.4, 129.9, 129.9, 130.7, 131.0, 131.3, 131.7, 132.2, 132.9, 137.0, 137.0, 138.2, 138.3, 139.8, 154.1, 158.0, 158.7; HRMS (ESI): *m*/*z* calcd for [**6**-H]$^+$ ($C_{60}H_{62}N_3O_5$): 904.4684; found: 904.4689.

4.3. *tert*-Butyl bis(4-bromobenzyl)carbamate (8)

Di-*tert*-butyl dicarbonate (570 mg, 2.6 mmol) and triethylamine (390 mg, 3.9 mmol) were added to a solution of the dibromide **7** (920 mg, 2.59 mmol) in MeOH (15 mL) and then the mixture was stirred at room temperature for 24 h. The organic solvent was evaporated under reduced pressure and the crude product purified chromatographically (SiO_2: CH_2Cl_2/hexane, 1:1) to yield the Boc-protected dibromide **8** as a yellow liquid (0.84 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.47 (s, 9H), 4.24 (br, 2H), 4.33 (br, 2H), 6.98–7.10 (br, 4H), 7.43 (d, *J*=8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=28.4, 48.7, 49.0, 80.4, 121.0, 128.8, 129.4, 131.5, 136.6, 155.5; HRMS (ESI): *m*/*z* calcd for ($C_{19}H_{21}Br_2NO_2$) [M+Na]: 475.98367; found: 475.98367.

4.4. *tert*-Butyl bis{4-[(trimethylsilyl)ethynyl]-benzyl}carbamate (9)

Tetrakis(triphenylphosphine)palladium(0) (101 mg, 0.09 mmol), copper iodide (16.7 mg, 0.09 mmol), and trimethylsilylacetylene (860 mg, 8.8 mmol) were added to a degassed solution of the dibromide **8** (1.0 g, 2.2 mmol) in triethylamine (15 mL) and then the mixture was heated at 40 °C for 12 h. After cooling to room temperature, the solution was partitioned between CH_2Cl_2 (10 mL) and H_2O (10 mL), the aqueous phase was extracted with CH_2Cl_2 (2×10 mL), and the combined organic phases were dried ($MgSO_4$), concentrated, and purified chromatographically (SiO_2: CH_2Cl_2/hexane, 1:3) to afford the carbamate **9** as a yellow liquid (893 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.24 (s, 18H), 1.44 (s, 9H), 4.24 (br, 2H), 4.36 (br, 2H), 7.00–7.18 (br, 4H), 7.39 (d, *J*=8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=0.4, 28.6, 49.4, 80.1, 93.9, 104.6, 121.7, 126.6, 127.3, 131.6, 137.7, 155.0; HRMS (ESI): *m*/*z* calcd for ($C_{29}H_{39}NO_2Si_2$) [M+Na]: 512.2417; found: 512.2417.

4.5. Ammonium salt 10-H·PF_6

K_2CO_3 (1 g, 7.2 mmol) was added to a solution of the carbamate **9** (890 mg, 1.8 mmol) in MeOH (20 mL). The mixture was stirred at room temperature for 30 min and partitioned between CH_2Cl_2 (20 mL) and H_2O (20 mL). The aqueous phase was washed with CH_2Cl_2 (2×20 mL) and then the combined organic phases were concentrated to give a yellow liquid, which was dissolved in a mixture of MeOH (15 mL) and trifluoroacetic acid (5 mL) and stirred at room temperature for 12 h. Saturated aqueous NH_4PF_6 solution (30 mL) was added to the mixture and then the organic solvent was evaporated. The precipitate was filtered off and washed with H_2O to afford the ammonium salt **10**-H·PF_6 as a white solid (610 mg, 85%). Mp=210–211 °C; ^{1}H NMR (400 MHz, CD_3CN): δ=3.50 (s, 2H), 4.23 (s, 4H), 7.44 (dd, *J*=8 Hz, 4H), 7.56 (d, *J*=8 Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN): δ=51.9, 80.3, 83.1, 124.2, 131.2, 131.7, 133.2; HRMS (ESI): *m*/*z* calcd for [**10**-H]$^+$ ($C_{18}H_{16}N$): 246.1277; found: 246.1283.

4.6. [2]Rotaxane 11-H·PF_6

After evaporating (under reduced pressure) the solvent from a mixture of the macrocycle **1** (108 mg, 0.25 mmol), the dialkyne **10**-H·PF_6 (100 mg, 0.25 mmol), and silica gel (208 mg) in CH_3NO_2 (10 mL), the solid obtained was mixed with 3,6-diphenyl-1,2,4,5-tetrazine (132 mg, 0.56 mmol) and ball-milled at room temperature for 1 h. The solid mixture was transferred to a 5 mL flask, heated at 100 °C for 3 days, and then purified chromatographically (SiO_2: MeOH/CH_2Cl_2, 2:98) to afford the [2]rotaxane **11**-H·PF_6 as a yellow solid (210 mg, 72%). Mp=195–196 °C; ^{1}H NMR (400 MHz, CD_3CN): δ=2.01 (t, *J*=7 Hz, 4H), 3.06–3.12 (m, 4H), 3.50–3.56 (m, 4H), 4.05 (s, 4H), 5.29 (s, 4H), 6.60–6.73 (m, 12H), 7.37–7.47 (m, 16H), 7.49–7.64 (m, 10H), 8.10 (s, 2H), 8.28 (dd, *J*=7, 2 Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN): δ=51.1, 68.2, 69.9, 71.2, 74.4, 116.7, 125.8, 127.9, 128.0, 129.1, 129.1, 129.2, 129.5, 129.9, 130.4, 130.7, 131.0, 131.6, 132.0, 136.9, 138.1, 138.2, 138.4, 139.5, 158.1, 158.6, 159.3; HRMS (ESI): *m*/*z* calcd for [**11**-H]$^+$ ($C_{72}H_{64}N_5O_5$): 1078.4902; found: 1078.4907.

4.7. [2]Rotaxane 12-H·PF_6

After evaporating (under reduced pressure) the solvent from a mixture of DB24C8 (390 mg, 0.3 mmol), the alkyne **2**-H·PF_6 (300 mg, 0.24 mmol), and silica gel (690 mg) in CH_3NO_2 (10 mL), the solid mixture obtained was mixed with 3,6-diphenyl-1,2,4,5-tetrazine (180 mg, 0.78 mmol), ball-milled at room temperature for 1 h, transferred to a 5 mL flask, and heated at 100 °C for 3 days. After cooling to room temperature, the resulting solid mixture was purified chromatographically (SiO_2: MeOH/CH_2Cl_2, 2:98) to afford the [2]rotaxane **12**-H·PF_6 as a white solid (560 mg, 73%). Mp=124–125 °C; ^{1}H NMR (400 MHz, CD_3CN): δ=1.23 (s, 9H), 3.42–3.57 (m, 8H), 3.63–3.80 (m, 8H), 3.98–4.06 (m, 8H), 4.54 (t, *J*=6 Hz, 2H), 4.74

(t, J=6 Hz, 2H), 6.78–6.84 (m, 8H), 7.13 (dd, J=6, 2 Hz, 2H), 7.19 (dd, J=8, 4 Hz, 4H), 7.22–7.40 (m, 7H), 7.52–7.63 (m, 5H), 7.86 (s, 1H), 8.23 (dd, J=8, 2 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ=31.3, 35.0, 52.4, 53.0, 68.5, 70.6, 71.0, 112.7, 121.4, 125.1, 125.5, 127.2, 128.3, 128.7, 129.2, 129.4, 129.5, 129.9, 130.2, 133.0, 136.2, 137.3, 137.4, 139.6, 147.4, 152.1, 157.5, 158.2 (two signals are missing, possibly because of signal overlap); HRMS (ESI): m/z calcd for [**12**-H]$^+$ ($C_{58}H_{66}N_3O_8$): 932.4850; found: 932.4850.

4.8. [2]Rotaxane 13-H·PF_6

After evaporating (under reduced pressure) the solvent from a mixture of DB24C8 (69 mg, 0.15 mmol), the dialkyne **10**-H·PF_6 (50 mg, 0.13 mmol), and silica gel (120 mg) in CH_3NO_2 (5 mL), the solid obtained was mixed with 3,6-diphenyl-1,2,4,5-tetrazine (180 mg, 0.78 mmol) and ball-milled at room temperature for 1 h. The resulting solid mixture was transferred to a 5 mL flask, heated to 100 °C for 3 days, and then purified chromatographically (SiO_2: $MeOH/CH_2Cl_2$, 2:98) to afford the [2]rotaxane **13**-H·PF_6 as a white solid (115 mg, 72%). Mp=117–118 °C; ^{1}H NMR (400 MHz, CD_3CN): δ=3.50 (s, 8H), 3.68–3.75 (m, 8H), 4.00–4.04 (m, 8H), 4.66 (t, J=6 Hz, 4H), 6.79 (s, 8H), 7.12 (dd, J=6, 2 Hz, 4H), 7.27–7.32 (m, 8H), 7.33–7.40 (m, 6H), 7.56–7.62 (m, 6H), 7.62–7.70 (br, 2H), 7.86 (s, 2H), 8.23 (dd, J=8, 2 Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN): δ=53.0, 68.9, 71.0, 71.4, 113.3, 122.1, 125.8, 127.9, 128.9, 129.4, 129.8, 130.2, 130.3, 130.6, 130.9, 133.1, 136.9, 138.0, 138.4, 139.3, 148.1, 158.3, 159.0; HRMS (ESI): m/z calcd for [**13**-H]$^+$ ($C_{70}H_{68}N_5O_8$): 1106.5062; found: 1106.5068.

Acknowledgements

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Supplementary data

Spectroscopic data (^{1}H and ^{13}C NMR) for all purified [2]rotaxanes. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.12.082.

References and notes

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10. A reaction temperature of 373 K was chosen because (i) the reaction proceeded extremely slowly at temperatures below 353 K and (ii) significantly lower yields were obtained for the reactions performed at temperatures above 383 K, possibly because of the rapid sublimation of diphenyltetrazine **5**.