Rotaxanes

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A Metal-Free "Threading-Followed-by-Shrinking" Protocol for Rotaxane Synthesis**

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The potential applicability of interlocked molecular switches or actuators in mesoscale molecular electronic devices has driven the development of new synthetic protocols for preparing these functional molecules.[1] Recently, in addition to the classical "threading-followed-by-stoppering",[2] slippage,[3] and clipping[4] approaches, a new "threading-followed-by-shrinking" protocol was described for [2]rotaxane synthesis. It employed a Pd^{2+} ion to chelate the salophen moiety of the macrocyclic unit in the corresponding [2]pseudorotaxane, thereby "shrinking" the size of the free space in the complexed macrocycle and interlocking the components in the form of a [2]rotaxane.[5] A more intuitive approach to "shrinking" would be decreasing the number of atoms in the skeleton of the macrocyclic component (Figure 1). Several challenges must be resolved to realize such a metal-free ring-shrinking protocol. 1) The rate of shrinking of the macrocycle in its complexed state should not be much slower than that in its free state. Therefore, the change in the structure of the shrinking motif in the macrocyclic unit should not disrupt most of the stabilizing interactions in the host–guest complex. One way to ensure such behavior would be for the non-shrinking portion of the macrocycle to be the primary source of stabilizing interactions toward the threadlike component. 2) A mild chemical reaction would be preferred for the shrinking of the ring skeleton of the macrocycle, so that the relatively weakly associated components of the [2]pseudorotaxane would not dissociate significantly during the transformation. 3) The sizes of the stopper of the dumbbell-shaped component and the cavity of the macrocycle must be finely tuned so that they can associate freely prior to performing the shrinking process, but not afterward. Herein, we report one such metal-free "threading-followed-by-shrinking" synthesis of a [2]rotaxane, mediated through photoextrusion[6] of SO_2 from the arylmethyl sulfone motif of the crown ether-like macrocyclic unit of a [2]pseudorotaxane featuring a dumbbell-shaped cycloheptyl-terminated dialkylammonium ion.

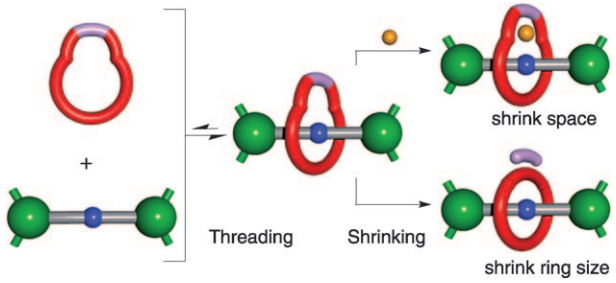
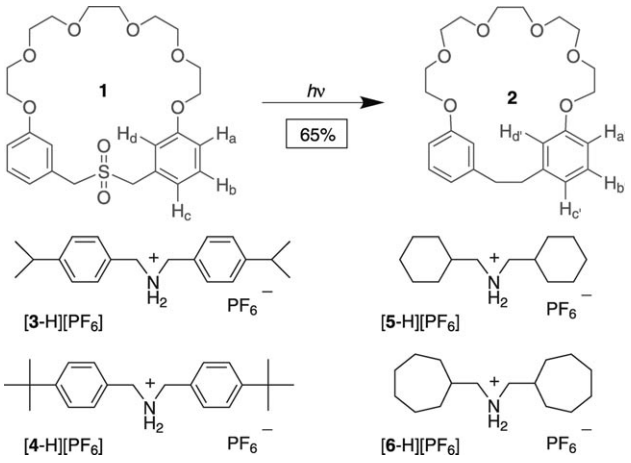


Figure 1. Cartoon representation of the concept of the metal-free "threading-followed-by-shrinking" protocol.

Macrocycles featuring oligo(ethylene glycol) units in their ring structures can form complexes with dialkylammonium ions with little assistance from the other components of their molecular structures.[7] Thus, we synthesized the macrocycle **1** (Scheme 1) to demonstrate the concept of metal-free shrinking; we expected its penta(ethylene glycol) unit to recognize dialkylammonium ions and its arylmethyl sulfone unit to extrude SO_2 under photochemical conditions, thereby decreasing the number of atoms in the ring skeleton. We chose photochemical extrusion as the crucial step in the synthesis because we suspected that this mild reaction would not disrupt the weakly associated components of the [2]pseudorotaxane in solution.



Scheme 1. Photoextrusion of SO_2 from macrocycle **1** and the structures of dumbbell-shaped guest dialkylammonium salts.

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To confirm that shrinking of the ring skeleton of macrocycle **1** through extrusion of SO_2 was possible, we irradiated a degassed solution of **1** in $C_6H_6/CH_2Cl_2/CH_3CN$ (5:5:1) at 273 K for 90 min; gratifyingly, we obtained the macrocycle **2** in 65% yield after column chromatography (Scheme 1). Next, it was necessary to select a suitable dumbbell-shaped guest with which to perform the shrinking reaction for [2]rotaxane synthesis. The macrocycles **1** and **2** are 25- and 24-membered-ring systems, respectively. Based on the knowledge that isopropylphenyl and cyclohexyl units are slippage stoppers[8] and that *p-tert*-butylphenyl and cycloheptyl units are true stoppers for dibenzo[24]crown-8 (DB24C8),[9] we synthesized a series of symmetric dialkylammonium salts (**3**–**6**-H·PF_6; Scheme 1) featuring various terminal groups to test whether they were capable of passing through the cavity of macrocycle **1** but not through that of macrocycle **2**.

The ^{1}H NMR spectrum of an equimolar mixture (5 mM) of macrocycle **1** and the threadlike salt **3**-H·PF_6 in $CDCl_3/CD_3CN$ (9:1) displayed three sets of signals: those of the two free components and their 1:1 complex. For the complex, the downfield shift of the signal of the methylene protons adjacent to the NH_2^+ center and the upfield shifts of the signals of the OCH_2CH_2 protons of the macrocycle, relative to the respective signals of the free species, are similar to those observed for [2]pseudorotaxanes prepared from DB24C8 and dibenzylammonium ions,[10] which suggests that the complex [**1**·**3**-H]$^+$ was likely to have a [2]pseudorotaxane geometry (Figure 2). Using the single-point method, we determined the association constant (K_a) for the complex formed between macrocycle **1** and the threadlike salt **3**-H·PF_6 to be 300 M^{-1}.[11] Under similar conditions (namely, standing at room temperature for several hours), we observed no signals for such a complex in the ^{1}H NMR spectrum of a mixture of **4**-H·PF_6 and macrocycle **1**. However, after heating the solution at 323 K for 2 h we detected a new set of signals representing a 1:1 complex, which suggests that the *p-tert*-butylphenyl termini of this threadlike salt were slippage stoppers for the macrocycle **1**. The cyclohexyl termini of the threadlike salt **5**-H·PF_6 passed through the cavity of macrocycle **1** smoothly (similar to the behavior of **3**-H·PF_6), whereas the corresponding threading of the cycloheptyl-terminated salt **6**-H·PF_6 had relatively slow kinetics, and required 1 h to reach equilibrium at room temperature, which suggests appropriate size complementarity for our proposed [2]rotaxane synthesis.

Next, we tested whether the "shrunk" macrocycle **2** could form [2]pseudorotaxane-like complexes with any of these four threadlike salts in $CHCl_3/CH_3CN$ (9:1). **3**-H·PF_6 rapidly formed a complex with macrocycle **2** at ambient temperature with a K_a value of 470 M^{-1}.[12] After heating their respective mixtures at 323 K for 2 h, ^{1}H NMR spectra revealed that the cyclohexyl groups of **5**-H·PF_6 were slippage stoppers for this macrocycle. In contrast, we observed no additional signals corresponding to [2]pseudorotaxanes in the spectra of the solutions of macrocycle **2** and the threadlike salts **4**-H·PF_6 and **6**-H·PF_6, which suggests that *p-tert*-butylphenyl and cycloheptyl units are both true stoppers for the macrocycle **2**. Thus, **6**-H·PF_6 appeared to be an ideal choice for use as a component in the shrinking reaction: its cycloheptyl units could penetrate through the cavity of macrocycle **1** at ambient temperature to form the corresponding [2]pseudorotaxane [**1**⊃**6**-H][PF_6] (Scheme 2), but the smaller macrocyclic unit **2** obtained after shrinking would be unlikely to pass over these stopper units.

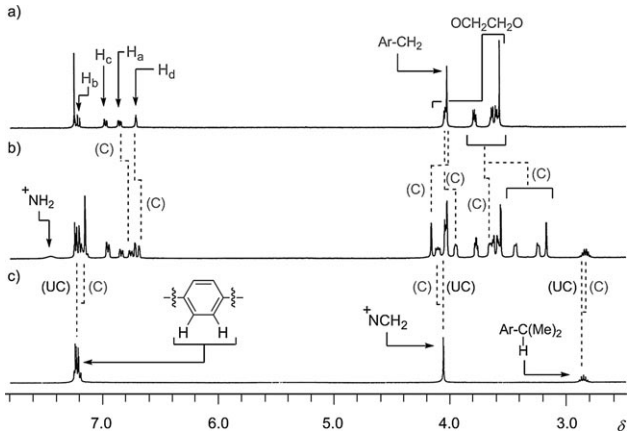
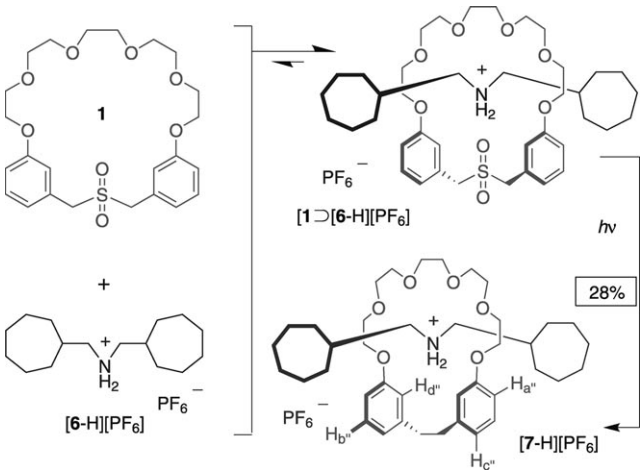


Figure 2. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ (9:1), 298 K) of a) macrocycle **1**, b) an equimolar mixture of **1** and threadlike salt **3**-H·PF_6 (5 mM), and c) **3**-H·PF_6. The descriptors (C) and (UC) refer to the signals of the components' complexed and uncomplexed states, respectively.



Scheme 2. The cycloheptyl units of **6**-H·PF_6 penetrate the cavity of macrocycle **1** to form the corresponding [2]pseudorotaxane [**1**⊃**6**-H]-[PF_6]. A shrinking reaction is performed by irradiating a solution of **1** and salt **6**-H·PF_6 to obtain the [2]rotaxane **7**-H·PF_6.

We performed the shrinking reaction by irradiating (254 nm) a $C_6H_6/CH_2Cl_2/CH_3CN$ (5:5:1) solution of macrocycle **1** (28.4 mM) and the threadlike salt **6**-H·PF_6 (70.9 mM) at 273 K for 90 min, and obtained the [2]rotaxane **7**-H·PF_6 in 28% yield after column chromatography (Scheme 2).[13] The ^{1}H NMR spectrum of this [2]rotaxane revealed significant downfield and upfield shifts of the ethylene glycol protons and the methylene protons adjacent to the NH_2^+ center, respectively, relative to those of their free components, which

suggests that [$^{+}$N–H···O] hydrogen bonding remained the most dominant noncovalent interaction in the system, with possible shielding of the methylene protons adjacent to the NH_2^+ center by the macrocycle's aromatic motifs (see Figure 3a–c). The spectrum of an equimolar mixture of salt

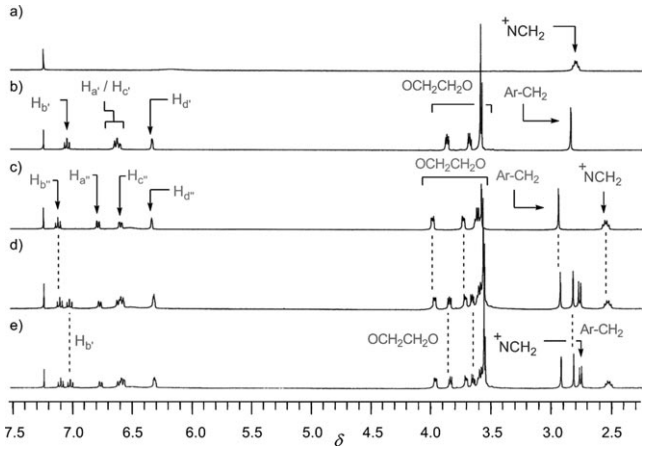


Figure 3. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3/CD_3CN$ (9:1), 298 K) of a) threadlike salt **6**-H·PF_6, b) macrocycle **2**, c) [2]rotaxane **7**-H·PF_6, d) an equimolar mixture of **2**, **6**-H·PF_6, and **7**-H·PF_6 (10 mM), and e) the solution in (d) after heating at 323 K for 16 h.

6-H·PF_6, macrocycle **2**, and the [2]rotaxane **7**-H·PF_6 in $CDCl_3/CD_3CN$ (9:1) revealed (Figure 3d) three sets of signals, of equal abundance, for the three species, which suggests that exchange of the components did not occur under these conditions. Heating this solution at 323 K for 16 h provided a spectrum similar to that measured prior to heating, thereby confirming that the [2]rotaxane had not assembled through slipping of threadlike salt **6**-H·PF_6 through macrocycle **2**.

Although the free radical intermediate in this photoextrusion reaction might have irreversibly combined to form the corresponding C–C bond within the solvent cage rapidly enough to retain the stereochemistry of the benzyl radicals,[14] it remained necessary for us to dismiss the possibility that the [2]rotaxane **7**-H·PF_6 was formed through clipping of the uncomplexed free radical intermediate about the recognition element in the threadlike salt. Thus, we irradiated (254 nm) a solution of threadlike salt **4**-H·PF_6 (70.9 mM) and macrocycle **1** (28.4 mM) in $C_6H_6/CH_2Cl_2/CH_3CN$ (5:5:1) for 90 min at 273 K. The ^{1}H NMR spectrum of the crude reaction product featured no signals for the corresponding [2]rotaxane, thus suggesting that the formation of a [2]pseudorotaxane prior to shrinking was an essential aspect of our rotaxane synthesis. Presumably, the lifetimes of the open-chain radical intermediates were not long enough for any potential formation of **7**-H·PF_6 through clipping. Thus, this [2]rotaxane was obtained almost exclusively through a process of threading of the rodlike component through the macrocycle and subsequent shrinkage of the macrocyclic component—a methodology that is conceptually different from those reported previously for synthesizing rotaxanes.[15]

We grew single crystals suitable for X-ray crystallography through liquid diffusion of toluene into a THF/CH_2Cl_2 solution of **7**-H·PF_6. The solid-state structure in Figure 4 reveals[16] the expected [2]rotaxane geometry, in which the rodlike portion of the dumbbell-shaped component has penetrated through the cavity of the macrocyclic component, with the $CH_2NH_2^+$ units hydrogen bonded to the oxygen atoms of the macrocyclic unit.

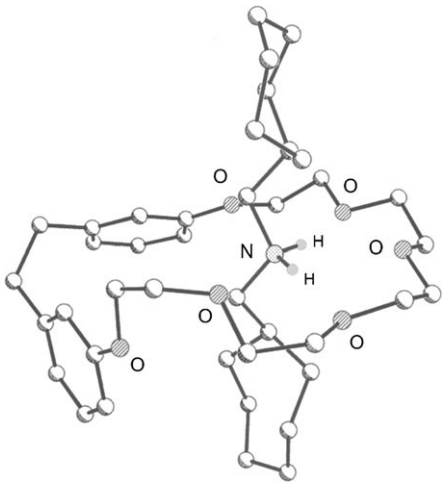


Figure 4. Ball-and-stick representation of the solid-state structure of the [2]rotaxane **7**-H$^+$.

In summary, we have developed a "threading-followed-by-shrinking" protocol for rotaxane synthesis under metal-free conditions, by employing photoextrusion to decrease the number of atoms in the ring skeleton of the macrocyclic component. This methodology adds to the repertoire of reactions available to the synthetic chemist for the construction of complicated interlocked structures.

Experimental Section

General method for the photoextrusion process: The photoextrusion reaction was performed using a Rayonet RPR-200 photoreactor containing 16 35 W, 254 nm lamps. The reaction mixture was placed in a quartz apparatus equipped with an internal cold finger.

7-H·PF_6: Macrocycle **1** (60.0 mg, 0.125 mmol) and threadlike salt **6**-H·PF_6 (120 mg, 0.312 mmol) were dissolved in a mixture of CH_2Cl_2, CH_3CN, and benzene (2.0:0.4:2.0 mL) and left at room temperature for 1 h before being irradiated under N_2 for 1.5 h. The organic solvents were evaporated under reduced pressure and the residue was purified by column chromatography (SiO_2; CH_2Cl_2/CH_3CN, 49:1) to afford the [2]rotaxane **7**-H·PF_6 as a white solid (28 mg, 28%). M.p. 176–178 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.00$–1.08 (m, 4H), 1.38–1.71 (m, 22H), 2.58–2.63 (m, 4H), 3.00 (s, 4H), 3.65–3.71 (m, 12H), 3.80–3.81 (m, 4H), 4.05–4.06 (m, 4H), 6.40 (s, 2H), 6.66 (d, $J = 8$ Hz, 2H), 6.83 (d, $J = 8$ Hz, 2H), 7.18 ppm (t, $J = 8$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 26.0, 28.4, 31.8, 35.4, 36.7, 55.5, 67.8, 71.1, 71.2, 71.3, 71.7, 110.0, 116.5, 122.4, 129.6, 142.9, 157.5$ ppm; HRMS (ESI): m/z [**7**-H]$^+$ $C_{40}H_{64}NO_6^+$ calcd: 654.4733; found: 654.4711.

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[16] Crystal data for [**7**-H·PF_6]: $[C_{40}H_{64}O_6N][PF_6]$; $M_r = 799.89$; triclinic; space group $P\bar{1}$; $a = 18.8647(4)$; $b = 19.8552(4)$; $c = 21.9993(3)$ Å; $V = 8190.8(3)$ Å^3; $\rho_{calcd} = 1.297$ g cm^{-3}; $\mu(Mo_{K\alpha}) = 1.221$ mm^{-1}; $T = 150(2)$ K; colorless needle; 29854 independent measured reflections; F^2 refinement; $R_1 = 0.1165$; $wR_2 = 0.3506$. CCDC 812242 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

