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Synthesis of a [2]Rotaxane Incorporating a "Magic Sulfur Ring" by the Thiol-Ene Click Reaction

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Abstract: The mild and highly efficient thiol-ene click reaction has been used to construct a rotaxane incorporating dibenzo-24-crown-8 (DB24C8) and a dibenzylammonium-derived thread in high yield under the irradiation of UV light. A rotaxane containing a disulfide linkage in the macrocycle was also synthesized by the thiol-ene click reaction. It has been demonstrated that the formation of the [2]rotaxane with the disulfide bond in the macrocycle occurs by a mechanism that is different to the threading-followed-by-stoppering process. The successful construction of a rotaxane directly from its constituent components, the macrocycle containing a disulfide linkage and the dibenzylammonium hexafluorophosphate salt, suggests that the space within the macrocycle incorporating the disulfide linkage is smaller than the phenyl unit and a plausible reaction mechanism has been proposed as follows: A small amount of the initiator forms two radicals upon the absorption of UV irradiation; the radicals act as a "key" to "unlock" the disulfide bond in the macrocycle. The resulting crown ether like moiety in the macrocycle is clipped around the ammonium ion center in the dumb-bell-shaped compound. The [2]rotaxane is generated upon recombination of the disulfide linkage.

Keywords: sulfur · macrocycles · reaction mechanisms · rotaxanes · template synthesis

Introduction

Rotaxanes are comprised of a macrocycle mechanically interlocked with a chemical "dumb-bell" component and have attracted considerable attention due to their potential applications in molecular electronic devices.[1] To develop a novel and functional artificial molecular machine, extensive efforts have been devoted to the development of efficient and convenient syntheses of mechanically interlocked molecules. The most straightforward protocol has probably been the "threading-followed-by-stoppering" approach. Various reactions have been successfully employed for this methodology, such as the Cu^{I}-mediated Huisgen 1,3-dipolar cycloaddition reaction of azides and alkynes,[2] reductive amination,[3] and the Witting reaction.[4] However, most of the reactions applied to the synthesis of these interlocked architectures have involved the use of metal catalysts or molecular sieves, which have sometimes limited their application. Thus, the search for reactions for the construction of mechanically interlocked molecules that are highly efficient, regioselective, and tolerant to various solvents remains a focus for scientists in this field.[5]

The thiol-ene coupling (TEC) reaction has many of the attributes of the click reaction, for example, quantitative yields, rapid reaction rates, mild reaction conditions, and compatibility with water and oxygen.[6] Importantly, the TEC reaction can be considered as an environmentally friendly process because it can proceed under benign conditions without a toxic metal catalyst. The TEC reaction has recently been recognized as a valuable tool for the synthesis of dendrimers,[7] polymer modification,[8] and polymerization reactions.[9] There are only a few examples of the use of the TEC reaction in the synthesis of small molecules, for example, in the synthesis of *S*-disaccharide and calix[4]arene-

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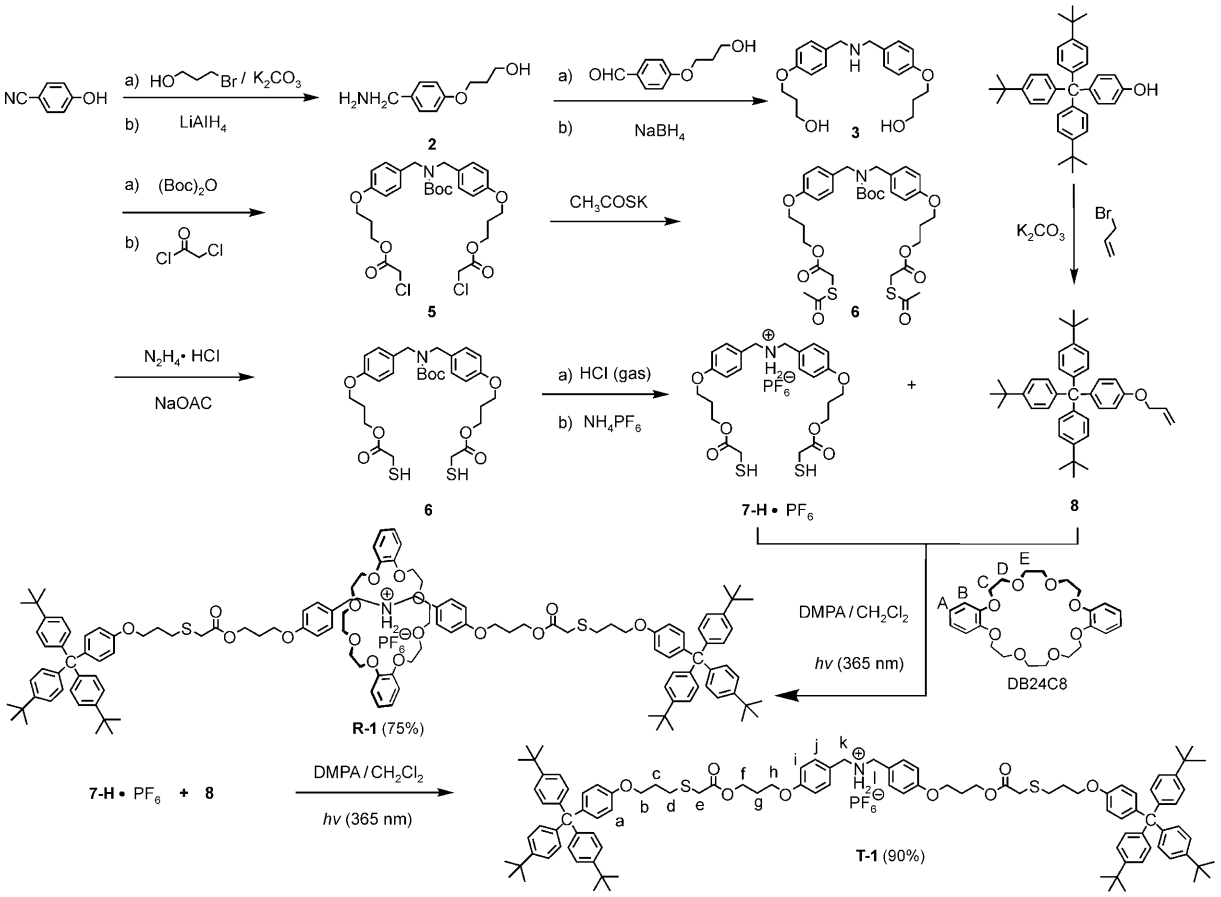
based *S*-glyco-clusters.[10] According to the literature,[11] the thiol-ene click coupling reaction can be induced photochemically or thermally, but the photochemically initiated coupling reaction was found to proceed with higher efficiency and required a shorter reaction time. Takata et al. have reported the synthesis of a [2]rotaxane by the thiol-ene coupling reaction under thermally initiated conditions,[12] however, the yield of the rotaxane was rather low and a reaction time of about 20 h was required. The low yield of the rotaxane seems to be a result of the low efficiency of the thermally initiated radical conjugated addition reaction, for example, the reaction took place at a high temperature, which can lead to the dissociation of pseudorotaxane complexes. On the other hand, the thiol-ene coupling reaction performed under irradiation close to visible light occurs in apolar solvent at room temperature without any base and does not produce tight-binding counteranions during the reaction process, which is advantageous for the stoppering of the DB24C8/ammonium cation pseudorotaxane complex.

Herein we describe a very efficient and mild method for the synthesis of a [2]rotaxane without the use of a metal catalyst. A novel rotaxane system incorporating a crown ether analogue bearing a disulfide linkage in the ring has also been constructed by the photoinitiated thiol-ene click reaction. However, it was demonstrated that the formation of this rotaxane may occur by a mechanism that is different to the threading-followed-by-stoppering process because the space within the macrocycle is smaller than the phenyl unit in the dibenzylammonium ion. The macrocycle with a disulfide linkage is rather interesting. It is stable in the presence of benzenethiol, which usually acts as a catalyst in thiol/disulfide interchange reactions,[13] but it becomes a "magic ring" under UV irradiation in the presence of the initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA).

Results and Discussion

The synthesis of [2]rotaxane **R-1** by using the thiol-ene click reaction as an end-capping procedure is outlined in Scheme 1. 4-Hydroxybenzonitrile was treated with 3-bromopropan-1-ol followed by reduction with $LiAlH_4$ to afford the benzylic primary amine. This was subsequently converted into **3** by condensation with 4-(3-hydroxypropoxy)benzaldehyde in the presence of anhydrous Na_2SO_4 followed by reduction of the resulting imine with $NaBH_4$ in methanol. After Boc protection, treatment with 2-chloroacetyl chloride afforded **5**. The reaction of compound **5** with potassium thioacetate resulted in the formation of the acetyl-protected thiol intermediate **6**. The introduction of two thiol glycolate



Scheme 1. Synthesis of [2]rotaxane **R-1** and thread **T-1**.

termini was accomplished by cleavage of the thioesters with hydrazine acetate, which can be generated in situ by ion exchange in DMF from considerably less expensive hydrazine hydrochloride acid and sodium acetate in high yield (95%).[8b] Removal of the Boc protecting group with a solution of HCl in ethyl acetate followed by anion exchange afforded the ammonium salt **7-H**·PF_6. [2]Rotaxane **R-1** was consequently synthesized by the addition of trace amounts of DMPA as initiator to a solution of **7-H**·PF_6, DB24CB, and stopper **8** in CH_2Cl_2. Irradiation with a UV lamp (λ_{ex} = 365 nm) at room temperature for 1 hour without making any effort to exclude oxygen and moisture afforded the target [2]rotaxane **R-1** in a yield of 75%. The results suggest that the TEC reaction can be carried out in apolar solvent, which could promote hydrogen-bonding interactions between the ammonium salt and DB24C8 to give a higher binding constant.[4a] The TEC reaction is also an example of total atom economy without the production of tight-binding counteranions that can destroy the [2]pseudorotaxane precursor.[4b] The thread **T-1** was synthesized in a manner similar to that described above for **R-1** in the absence of DB24C8.

The MALDI-TOF mass spectrum of **R-1** shows a sharp peak at m/z = 2031.9 $[M-PF_6^-]^+$ (see the Supporting Information), which is a characteristic of the interlocked molecule. As shown in Figure 1, the ^{1}H NMR spectroscopic data of [2]rotaxane **R-1** reveals significant chemical shifts relative to the separate components **T-1** and DB24C8. As expected, the biggest change in chemical shifts is the downfield shift of 0.50 ppm of the protons H_k adjacent to the ammonium unit compared with those in the free thread **T-1** due to their involvement in hydrogen bonding with DB24C8.[14] The phenylene proton H_i in the thread experiences an upfield shift (0.14 ppm) in **R-1** as a result of the aromatic shielding effect of DB24C8. Upfield shifts of 0.17 and 0.38 ppm for the polyether protons H_D and H_E of DB24C8, respectively, are observed, which can be ascribed to a combination of C–H·· O and N^+–H·· O hydrogen-bonding interactions.[4b]

Inspired by the successful synthesis of the [2]rotaxane **R-1**, to determine the generality and efficiency of this method

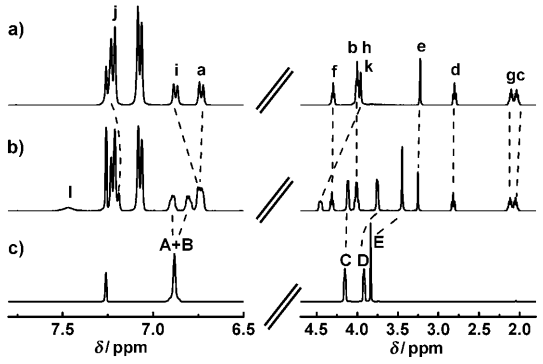
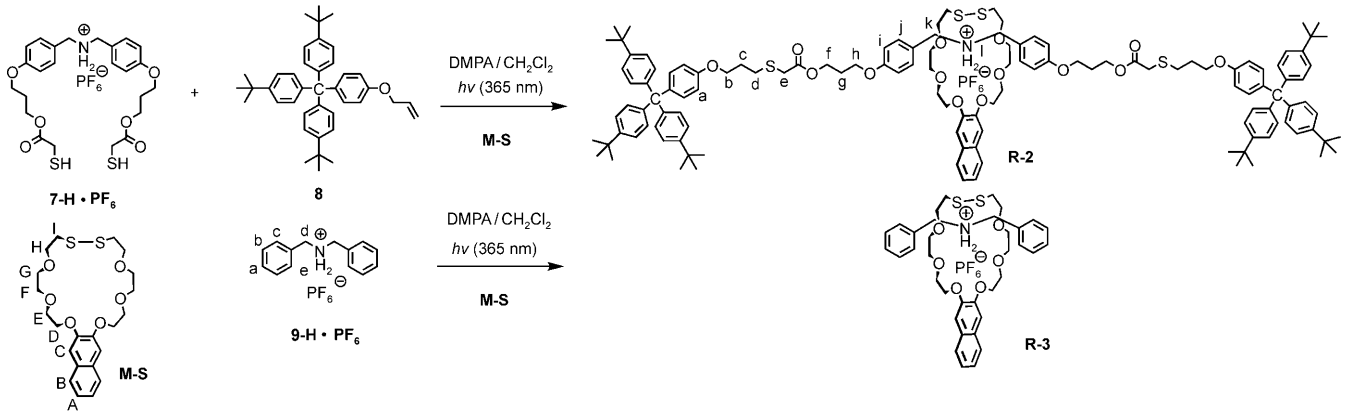


Figure 1. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 4×10^{-3} M, 298 K) of a) **T-1**, b) **R-1**, and c) DB24C8. The letters corresponding to the protons are shown in Scheme 1.

we were interested in testing whether we could stopper a weakly binding crown ether/ammonium cation pseudorotaxane complex such as the crown ether analogue possessing a disulfide linkage in the ring (M-S). The macrocycle M-S was obtained in high yield by following a literature procedure.[13a] Shinkai et al. have reported that the binding ability of M-S towards alkali metal cations is much smaller than that of a crown ether because the incorporated disulfide bond has no coordination ability and an unfavorable distorted conformation.[15]

[2]Rotaxane **R-2** was synthesized (Scheme 2) in a manner similar to that described above for **R-1**. After irradiation for 1 hour, the interlocked molecule **R-2** was obtained in a yield of 30% after chromatography.

The presence of a signal at m/z = 2037.4 in the MALDI-TOF mass spectrum, which corresponds to **R-2**$^+$ after loss of the PF_6^- unit, supports the presence of the [2]rotaxane **R-2**. The interlocked nature of the [2]rotaxane **R-2** was also corroborated by the ^{1}H NMR spectra of the uncomplexed dumb-bell-shaped thread and the rotaxane, as shown in Figure 2. The characteristic proton close to the ammonium ion center H_k experiences a significant downfield shift of 0.62 ppm, which confirms the presence of the macrocyclic M-S moiety around the ammonium unit in rotaxane **R-2**.



Scheme 2. Synthesis of [2]rotaxanes **R-2** and **R-3.**

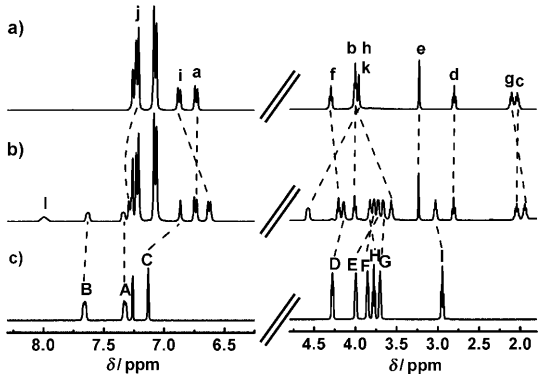


Figure 2. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 4×10^{-3} M, 298 K) of a) **T-1**, b) **R-2**, and c) M-S. The letters corresponding to the protons are shown in Scheme 2.

The proton H_f is shifted upfield slightly (0.09 ppm) whereas the upfield shift of proton H_h is more pronounced (0.44 ppm) as a result of the aromatic shielding effect of the M-S. The signal corresponding to phenylene proton H_i exhibits a substantial upfield shift (0.25 ppm) due to the aromatic shielding effect of the macrocycle. An upfield shift (0.26 ppm) is observed at the same time for the signal of H_C. These results are due to the π···π stacking interaction between the macrocycle and the phenylene spacers in thread **T-1**. The methylene protons H_D, H_E, and H_F within the M-S are shifted upfield by 0.14, 0.27, and 0.08 ppm, respectively, as a result of weak C–H···O and N^+–H···O hydrogen bonds, whereas the signals for protons H_I and H_H are shifted downfield by 0.08 and 0.04 ppm, respectively. The broad signal for the proton H_l of the NH_2^+ center also confirms the existence of N^+–H···O hydrogen bonding between this center and the M-S.[4b]

All the results support the presence of [2]rotaxane **R-2** containing a crown ether analogue with a disulfide linkage in the ring. However, to our surprise, as shown in Figure 3, we did not observe significant shifts of the signals in the ^{1}H NMR spectra (298 K) of an equimolar mixture of macrocycle **M-S** and the dibenzylammonium hexafluorophosphate salt **7-H**·PF_6 whereas a dramatic change was observed in the ^{1}H NMR spectra (298 K) of an equimolar mixture of DB24C8 and **7-H**·PF_6 (Figure 4). It has been reported that

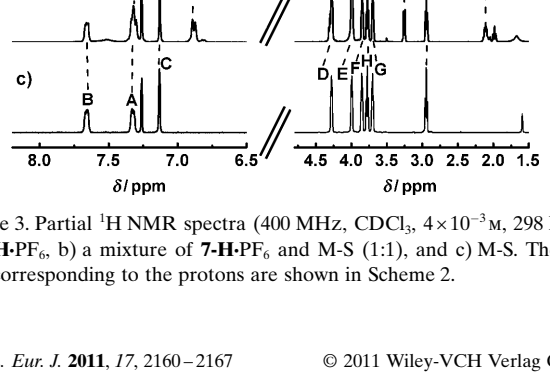


Figure 3. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 4×10^{-3} M, 298 K) of a) **7-H**·PF_6, b) a mixture of **7-H**·PF_6 and M-S (1:1), and c) M-S. The letters corresponding to the protons are shown in Scheme 2.

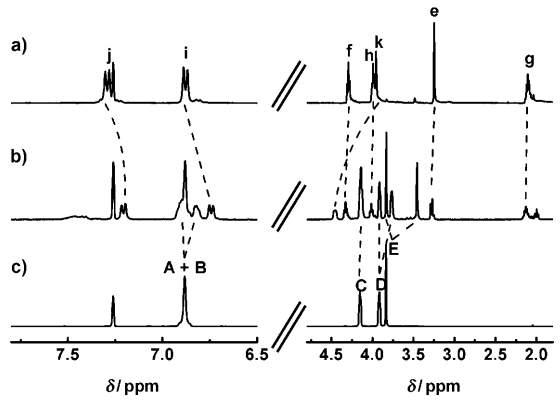


Figure 4. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 4×10^{-3} M, 298 K) of a) **7-H**·PF_6, b) a mixture of **7-H**·PF_6 and DB24C8 (1:1), and c) DB24C8. The letters corresponding to the protons are shown in Scheme 1.

the ring size of the macrocycle M-S is similar to or slightly larger than 21-crown-7[15] and that the phenyl groups are sufficient to trap the 21-crown-7 on the axle containing the ammonium cation to form a [2]rotaxane.[16] That is, there is no significant interaction between the macrocycle M-S and the ammonium ion **7-H**·PF_6 probably because the M-S ring is smaller than the phenyl unit and the dibenzylammonium unit cannot thread through the cavity of M-S to form a pseudorotaxane. All the results indicate that the formation of [2]rotaxane **R-2** might occur by a mechanism that is different to the threading-followed-by-stoppering process.

To test our hypothesis we prepared dibenzylammonium hexafluorophosphate salt **9-H**·PF_6 (Scheme 2). The two thiol glycolate termini of **9-H**·PF_6 are not present thereby preventing interference of the thiol glycolates and making the system simpler. When a solution of macrocycle M-S and the dibenzylammonium hexafluorophosphate salt **9-H**·PF_6 in CH_2Cl_2 (the noncompeting solvent maximizes the strength of the intercomponent hydrogen bonding) was exposed to UV irradiation for 1 hour in the presence of 0.5 equiv. of DMPA as the initiator, [2]rotaxane **R-3** was obtained (shown in Scheme 2) in a yield of 38%.

The MALDI-TOF mass spectrum (see the Supporting Information) and the ^{1}H NMR spectra of the dibenzylammonium hexafluorophosphate salt **9-H**·PF_6, rotaxane **R-3**, and M-S in chloroform confirm the interlocked structure. As shown in Figure 5, the ^{1}H NMR spectroscopic data of [2]rotaxane **R-3** reveals significant chemical shifts relative to the dibenzylammonium hexafluorophosphate salt **9-H**·PF_6 and the ring M-S. The signal of benzylic proton H_d has been shifted to a lower field by 0.71 ppm. Such a downfield shift of the benzylic proton with a neighboring secondary ammonium group has been observed in most rotaxanes consisting of a crown ether analogue and a secondary ammonium salt.[4] As described above, protons H_a and H_b experience

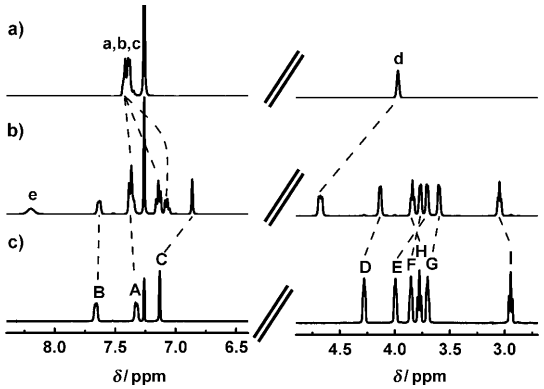
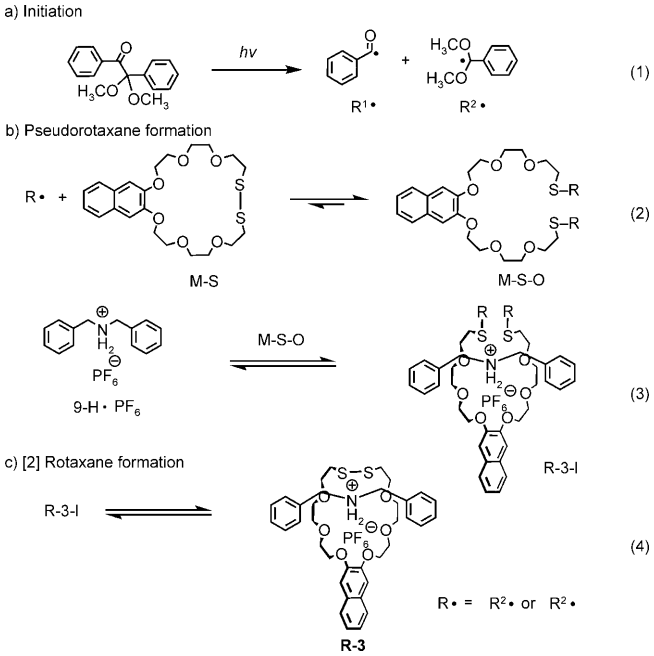


Figure 5. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 4×10^{-3} M, 298 K) of a) **9-H·**PF_6, b) **R-3**, and c) M-S. The letters corresponding to the protons are shown in Scheme 2.

upfield shifts of 0.33 and 0.25 ppm, respectively, and also proton H_C is shifted upfield by 0.27 ppm as a result of the aromatic shielding effect. The signals of protons H_D, H_E, H_F, and H_G of the M-S unit of **R-3** are shifted upfield by 0.15, 0.28, 0.09, and 0.1 ppm, respectively, which are characteristic of a crown ether analogue positioned around the ammonium center of **9-H·**PF_6 and stabilized by C–H···O and N^+–H···O hydrogen bonds. The broad signal from the proton H_e of the NH_2^+ center also supports the existence of N^+–H···O hydrogen bonding between this center and the M-S unit.[4b]

These results indicate that the macrocycle with a disulfide linkage is smaller than the phenyl unit but can be trapped by the phenyl unit to form rotaxane. A possible mechanism for the formation of [2]rotaxane **R-3** is depicted in Scheme 3. The initiator DMPA forms two different radicals upon absorption of UV light [Eq. (1)]. Either or both radicals may attack the disulfide linkage of macrocycle M-S leading to three different intermediates. The radicals act as a "key" to "unlock" the disulfide bond. The crown ether like moiety in the "unlocked" M-S is clipped around the dibenzylammonium hexafluorophosphate salt **9-H·**PF_6 as a result of the template effect of the ammonium ion center [Eqs. (2) and (3)]. After elimination of the R^1 or R^2 groups, [2]rotaxane **R-3** is generated by recombination of the disulfide linkage in M-S [Eq. (4)]. The reaction mechanism is currently being investigated in detail to find, for example, the different stabilities of the three kinds of intermediates. The macrocycle M-S, which contains a dynamic reversible covalent bond, the disulfide bond, is usually called a "magic ring".[17] Although the macrocycle with the disulfide linkage is stable in the presence of benzenethiol, which is usually a catalyst in thiol/disulfide interchange reactions,[13] it can be "unlocked" by irradiation with UV light in the presence of the initiator DMPA. This can result in the thermodynamically controlled synthesis of a dynamic [2]rotaxane directly from its constituent components under appropriate conditions. [17a] (The thermodynamically controlled synthesis of rotaxane **R-3** by "magic-ring" clipping is demonstrated in the Supporting Information). Note that no special manipulation is needed to remove the initiator. Compared with other well-known reversible reactions, this method is more advantageous and convenient because the removal of UV irradiation is all that is required to lock the product. In contrast, the olefin metathesis method requires the reaction-specific catalyst to be removed to isolate the product.[18] A fast reduction of the imine bond to obtain the kinetically stable product is necessary when the imine bond acts as a reversible linker in the formation of dynamic interlocked molecules because this reversible process is fast at room temperature.[19]



Scheme 3. Possible mechanism for the formation of [2]rotaxane **R-3**.

All the above suggest that the formation of [2]rotaxane **R-2** by the thiol-ene click reaction occurs by a process that is not a threading-followed-by-stoppering process but a clipping one. The reason for the low yield of [2]rotaxane **R-2** is the weak binding ability of the M-S and dibenzylammonium unit, on the other hand the formation of polydisulfide. In fact, the thiol-ene click reaction and the reversible cleavage of the disulfide bond can both be initiated by the photoinitiator DMPA upon absorption of UV light and these two reactions can occur simultaneously. On this basis, we can synthesize [2]rotaxanes with a disulfide linkage in the macrocycle and modify it by the thiol-ene click reaction in one pot upon irradiation with UV light in the presence of the photoinitiator DMPA.

Conclusion

The efficient end-capping synthesis of a [2]rotaxane has been achieved by the photoinitiated thiol-ene click reaction, which is promoted by irradiation at close to visible light. This may provide a route to the construction of other complicated interlocked structures. In addition, a rotaxane con-

taining a disulfide linkage in the macrocycle has been synthesized by the thiol-ene click reaction and it has been demonstrated to occur by a "magic ring" clipping process. This approach can be used to construct a thermodynamically controlled but kinetically robust rotaxane systems. The reversible cleavage of the disulfide linkage upon irradiation of UV light in the presence of a photoinitiator has provided a novel approach to the synthesis of interlocked structures through "dynamic" covalent bonds under thermodynamic control. Further work exploring the use of the "magic ring" to construct complex interlocked architectures is underway.

Experimental Section

General methods: Unless stated otherwise, all reagents were purchased from Aldrich Chemicals and used without further purification. Solvents were purified according to standard laboratory methods. Chromatographic separations were performed on silica gel (200–300 mesh). Reactions were monitored by thin-layer chromatography (TLC) on glass plates coated with SiO_2 F254 and visualized by UV light ($\lambda = 254$ and 365 nm). ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 400 or 600 instrument at a constant temperature of 25 °C. All chemical shifts are reported in parts per million (ppm) from low to high field and are referenced to TMS. MALDI-TOF mass spectra were recorded on a Bruker Biflex III MALDI-TOF spectrometer. High-resolution mass spectra were recorded on a GCT-MS Micromass UK or ESI Bruker Daltonics, APEXII, FT-ICRMS spectrometer. The household UV lamp apparatus was equipped with three 8 W tubes (1.5×29 cm each, $\lambda_{ex} = 365$ nm). The commercially available photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) was used without further purification.

Compound 1: 4-Hydroxybenzonitrile (10 g, 84.0 mmol) and 3-bromopropan-1-ol (9.7 g, 69.8 mmol) were dissolved in dry acetonitrile (250 mL) and heated at reflux overnight in the presence of anhydrous K_2CO_3 (38.5 g, 279.2 mmol) under nitrogen. The mixture was filtered and the solvent removed under vacuum. The crude product was dissolved in CH_2Cl_2 and washed with an aqueous NaOH solution (3×250 mL) and water (2×250 mL). The combined organic layers were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by chromatography (CH_2Cl_2) to afford compound **1** as a viscous liquid (11.0 g, 89%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 7.56 (d, $J = 8.1$ Hz, 2H), 6.94 (d, $J = 8.1$ Hz, 2H), 4.15 (t, $J = 6.0$ Hz, 2H), 3.84 (t, $J = 5.8$ Hz, 2H), 2.08–2.02 (m, 2H), 1.78 ppm (s, 1H); ^{13}C NMR (100 MHz , $CDCl_3$, 25 °C, TMS): $\delta = 162.32$, 134.09, 119.32, 115.31, 103.95, 65.60, 59.54, 31.86 ppm; HRMS (EI): m/z: calcd for $C_{10}H_{11}NO_2$: 177.0790 $[M]^+$; found: 177.0792.

Compound 2: Compound **1** (10 g, 56.5 mmol) was dissolved in anhydrous tetrahydrofuran (300 mL). Then $LiAlH_4$ (3.2 g, 84.2 mmol) was added cautiously at 0 °C under a nitrogen atmosphere. The mixture was stirred at room temperature for 2 h. After that the reaction mixture was heated at reflux overnight. Water was added cautiously after the system had been cooled to room temperature to quench the excess $LiAlH_4$. After filtration, the solution was concentrated under reduced pressure to afford **2** as a slightly yellow solid (6.94 g, 68%). The compound was not purified further for use in the next reaction.

Compound 3: A solution of compound **2** (2.09 g, 11.5 mmol) in ethanol (50 mL) was added dropwise to a degassed solution of 4-(3-hydroxypropoxy)benzaldehyde (3.12 g, 17.3 mmol) in anhydrous EtOH/THF (40 mL, 3:1). Then anhydrous Na_2SO_4 was added and the resulting mixture was stirred for 12 h at room temperature. Then $NaBH_4$ (4.37 g, 115 mmol) was added to the mixture at 0 °C, which was stirred for 4 h after warming to room temperature. Water (10 mL) was added carefully to quench the excess $NaBH_4$. The solvent was then evaporated and the reaction mixture was partitioned between water and CH_2Cl_2 (3×100 mL). The aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were dried over Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by column chromatography (CH_2Cl_2/MeOH, 15:1) to afford **3** as a white solid in 71% yield. M.p. 99.6–101.2 °C; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.24$ (d, $J = 8.4$ Hz, 4H), 6.87 (d, $J = 8.4$ Hz, 4H), 4.12 (t, $J = 5.9$ Hz, 4H), 3.87 (t, $J = 5.8$ Hz, 4H), 3.72 (s, 4H), 2.07–2.01 (m, 4H), 1.67 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 157.95$, 132.85, 129.51, 114.54, 66.01, 60.71, 60.67, 52.59, 32.17 ppm; MS (EI) m/z: 345 $[M]^+$; elemental analysis calcd (%) for $C_{20}H_{27}NO_4$: C 69.54, H 7.88, N 4.05; found: C 69.32, H 7.99, N 4.03.

Compound 4: Compound **3** (5 g, 14.5 mmol) was dissolved in CH_2Cl_2 (200 mL) and then a solution of di-*tert*-butyl dicarbonate (3.80 g, 17.4 mmol) in CH_2Cl_2 (20 mL) was added dropwise under nitrogen at 0 °C. The reaction mixture was stirred at room temperature overnight. Then the mixture was washed with water (2×100 mL), the organic phase was dried over Na_2SO_4, and the CH_2Cl_2 was removed in vacuo to afford the product in 98% yield after purification by column chromatography (CH_2Cl_2/MeOH, 30:1). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.09$ (s, 4H), 6.83 (d, $J = 7.8$ Hz, 4H), 4.26 (d, $J = 30.2$ Hz, 4H), 4.05 (t, $J =$ 5.9 Hz, 4H), 3.78 (t, $J = 5.5$ Hz, 4H), 3.15 (s, 2H), 2.01–1.96 (m, 4H), 1.48 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 158.05$, 155.98, 129.95, 129.20, 128.69, 114.44, 80.02, 65.27, 59.59, 48.37, 48.10, 32.00, 28.40 ppm; HRMS (EI): m/z: calcd for $C_{25}H_{35}NO_6$: 445.2464 $[M]^+$; found: 445.2471.

Compound 5: Compound **4** (1.96 g, 4.39 mmol) and Et_3N (1.78 g, 17.6 mmol) were dissolved in CH_2Cl_2 (100 mL). Then a solution of 2-chloroacetyl chloride (1.98 g, 17.56 mmol) in CH_2Cl_2 (20 mL) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 1 h and washed with water (2×50 mL). The organic layer was dried over Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate, 2:1) to afford compound **5** in 95% yield. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.13$ (s, 4H), 6.84 (d, $J = 7.7$ Hz, 4H), 4.40 (t, $J =$ 6.2 Hz, 4H), 4.28 (d, $J = 22.2$ Hz, 4H), 4.06–4.04 (m, 8H), 2.19–2.13 (m, 4H), 1.50 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta =$ 167.17, 157.85, 155.83, 130.33, 129.28, 128.77, 114.42, 79.81, 64.01, 63.00, 48.31, 48.26, 48.06, 40.78, 28.41 ppm; HRMS (EI) : m/z: calcd for $C_{29}H_{37}NO_8C_{12}$: 597.1896 $[M]^+$; found: 597.1903.

Compound 6: Potassium thioacetate (380 mg, 3.33 mmol) was added to a solution of compound **5** (1 g, 1.67 mmol) in acetone (10 mL). Then the mixture was stirred at room temperature for 1 h. Acetone was removed under reduced pressure after filtration. Then the crude product was purified by chromatography on SiO_2 with petroleum ether/ethyl acetate (2:1) to afford compound **6** in 95% yield. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.12$ (s, 4H), 6.85 (d, $J = 7.9$ Hz, 4H), 4.35–4.24 (m, 8H), 4.04 (t, $J = 5.9$ Hz, 4H), 3.70 (s, 4H), 2.36 (s, 6H), 2.14–2.11(m, 4H), 1.50 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 193.49$, 168.48, 157.85, 155.72, 130.16, 129.19, 129.17, 128.66, 114.37, 79.68, 64.02, 62.45, 48.23, 48.18, 48.00, 47.95, 31.31, 29.91, 28.37, 28.35 ppm; HRMS (EI): m/z: calcd for $C_{33}H_{43}NO_{10}S_2$: 677.2328 $[M]^+$; found: 677.2335.

Compound 7: Hydrazine monohydrochloride (808 mg, 11.8 mmol) and sodium acetate (1.93 g, 23.59 mmol) were added to a solution of compound **6** (1 g, 1.47 mmol) in anhydrous *N,N*-dimethylformamide (10 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature for 4 h. The product was extracted with ethyl acetate (2×100 mL) after the addition of water (100 mL). The organic phase was washed with water (6×100 mL). Then the organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. Compound **7** was afforded in 95% yield after chromatography on SiO_2 (petroleum ether/ethyl acetate, 2:1). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.12$ (s, 4H), 6.85 (d, $J =$ 7.6 Hz, 4H), 4.36–4.31 (m, 8H), 4.05 (t, $J = 5.7$ Hz, 4H), 3.26 (d, $J =$ 8.2 Hz, 4H), 2.16–2.13 (m, 4H), 1.99 (t, $J = 8.2$ Hz, 2H), 1.50 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 170.60$, 157.83, 155.73, 130.23, 129.20, 129.03, 128.96, 128.90, 128.70, 114.38, 79.70, 64.09, 62.35, 48.02, 28.41, 28.37, 26.30 ppm; HRMS (EI): m/z: calcd for $C_{29}H_{39}NO_8S_2$: 593.2117 $[M]^+$; found: 593.2124.

7-H·PF$_6$: Compound **7** (2 g, 3.36 mmol) was dissolved in a solution of HCl in ethyl acetate (150 mL; prepared by bubbling dry HCl into dry

ethyl acetate) under nitrogen. The mixture was stirred at room temperature until the reaction was complete, as determined by TLC (typically 3 h). Then the solvent was evaporated in vacuo to afford a white solid. This solid was dispersed in CH_2Cl_2 (50 mL) and a solution of NH_4PF_6 (1.1 g, 6.75 mmol) in water (50 mL) was added. The biphasic solution was stirred vigorously for 2 h and the aqueous layer was extracted with CH_2Cl_2 (2×50 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated to give the product in quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.29 (d, J = 8.2 Hz, 4H), 6.88 (d, J = 8.2 Hz, 4H), 4.29 (t, J = 6.2 Hz, 4H), 3.99 (t, J = 5.8 Hz, 4H), 3.96 (s, 4H), 3.25 (s, 4H), 2.12–2.08 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 171.22, 159.61, 131.33, 123.65, 115.21, 64.37, 62.59, 50.52, 28.50, 26.56 ppm; HRMS (ESI): m/z: calcd for $C_{24}H_{32}F_6NO_6PS_2$: 494.1671 [M-PF_6^-]$^+$; found: 494.1645.

Compound 8: Tris(4-*tert*-butylphenyl)(4-hydroxyphenyl)methane[20] (2.5 g, 4.96 mmol) and allyl bromide (1.8 g, 14.9 mmol) were dissolved in dry acetonitrile (100 mL) and heated at reflux overnight in the presence of anhydrous K_2CO_3 (2.06 g, 14.9 mmol) under nitrogen. The mixture was filtered and the solvent removed under vacuum. The crude product was dissolved in CH_2Cl_2 and washed with water three times. The combined organic layers were dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by chromatography (petroleum ether/EtOAC, 30:1) to afford compound **8** as a white solid (2.62 g, 97%). M.p. 265.3–266.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.23 (d, J = 7.3 Hz, 6H), 7.08 (d, J = 7.4 Hz, 8H), 6.78 (d, J = 7.6 Hz, 2H), 6.09–6.02 (m, 1H), 5.41 (d, J = 17.3 Hz, 1H), 5.27 (d, J = 10.5 Hz, 1H), 4.51 (d, J = 5.2 Hz, 2H), 1.30 ppm (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 156.61, 148.44, 144.32, 139.88, 133.66, 132.40, 130.92, 124.18, 117.70, 113.35, 68.87, 63.23, 34.44, 31.56 ppm; MS (EI): m/z: 544 [M]$^+$; elemental analysis calcd (%) for $C_{40}H_{48}O$: C 88.18, H 8.88; found: C 88.19, H 8.88.

Thread T-1: The reaction was carried out in a quartz cell (diameter: 1 cm; wall thickness: 1 cm) sealed with a natural rubber plug located 5.5 cm away from the UV lamp. DMPA (5.6 mg, 0.022 mmol) was added to a solution of compound **7-H**·PF_6 (28 mg, 0.044 mmol) and compound **8** (59.6 mg, 0.11 mmol) in anhydrous CH_2Cl_2 (2 mL). The reaction mixture was irradiated at room temperature for 1 h under a nitrogen atmosphere without stirring. After concentration, the crude product was purified by chromatography (CH_2Cl_2/MeOH = 20:1) to afford thread **T-1** as a white solid (68 mg, 90%). M.p. 125.4–125.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.22 (d, J = 8.2 Hz, 14H), 7.07 (d, J = 8.1 Hz, 16H), 6.88 (d, J = 8.1 Hz, 4H), 6.73 (d, J = 8.4 Hz, 4H), 4.30 (t, J = 6.2 Hz, 4H), 4.02–3.99 (m, 8H), 3.96 (s, 4H), 3.23 (s, 4H), 2.80 (t, J = 7.1 Hz, 4H), 2.14–2.09 (m, 4H), 2.05–2.00 (m, 4H), 1.30 ppm (s, 54H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 170.66, 159.65, 156.68, 148.43, 144.26, 139.87, 132.39, 131.18, 130.85, 124.17, 123.79, 115.29, 113.12, 65.96, 64.37, 63.18, 62.21, 50.86, 34.41, 33.78, 31.52, 29.50, 28.90, 28.60 ppm; MS (MALDI-TOF): m/z: 1606.1 [M−PF_6^-+Na]$^+$, 1622.2 [M−PF_6^-+K]$^+$; elemental analysis calcd (%) for $C_{104}H_{128}F_6NO_8PS_2$: C 72.24, H 7.46, N 0.81; found: C 72.46, H 7.51, N 0.86.

[2]Rotaxane R-1: The reaction was carried out as described for the preparation of thread **T-1**. DMPA (5.6 mg, 0.022 mmol) was added to a solution of **7-H**·PF_6 (28 mg, 0.044 mmol), compound **8** (59.6 mg, 0.11 mmol), and dibenzo-24-crown-8 (DB24C8; 29.4 mg, 0.066 mmol) in anhydrous CH_2Cl_2 (2 mL). The reaction mixture was irradiated at room temperature for 1 h under a nitrogen atmosphere without stirring. After concentration, the crude product was purified by chromatography (CH_2Cl_2/MeOH, 30:1) to afford rotaxane **R-1** as a white solid (71.5 mg, 75%). M.p. 127.8–128.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.47 (s, 2H), 7.23–7.19 (m, 16H), 7.07 (d, J = 7.8 Hz, 16H), 6.90–6.89 (m, 4H), 6.81–6.80 (m, 4H), 6.75–6.73 (m, 8H), 4.47–4.45 (m, 4H), 4.31 (t, J = 6.2 Hz, 4H), 4.12–4.11 (m, 8H), 4.03–3.99 (m, 8H), 3.76–3.75 (m, 8H), 3.45 (m, 8H), 3.25 (s, 4H), 2.82 (t, J = 6.9 Hz, 4H), 2.13–2.10 (m, 4H), 2.07–2.05 (m, 4H), 1.29 ppm (s, 54H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 170.47, 159.33, 156.63, 148.32, 147.53, 144.17, 139.73, 132.27, 130.78, 130.75, 124.15, 124.13, 124.12, 124.10, 124.05, 124.02, 123.85, 121.73, 114.54, 113.04, 112.80, 70.75, 70.20, 68.27, 65.90, 64.27, 63.08, 62.23, 52.00, 34.33, 34.31, 34.30, 33.66, 31.52, 31.49, 31.48, 31.46, 31.45, 31.41, 31.38, 31.36, 31.35, 31.33, 31.32, 31.30, 31.29, 29.70, 29.40, 28.80, 28.51 ppm; MS (MALDI-TOF): m/z 2031.9 [M−PF_6^-]$^+$; elemental analysis calcd (%) for $C_{128}H_{160}F_6NO_{16}PS_2$: C 70.60, H 7.41, N 0.64; found: C 70.91 , H 7.58, N 0.66.

[2]Rotaxane R-2: The reaction was carried out as described for the preparation of thread **T-1**. DMPA (5.3 mg, 0.021 mmol) was added to a solution of compound **7-H**·PF_6 (26 mg, 0.041 mmol), compound **8** (55.3 mg, 0.10 mmol), and macrocycle M-S[13a] (22.1 mg, 0.049 mmol) in anhydrous CH_2Cl_2 (2 mL). The reaction mixture was irradiated at room temperature for 1 h under a nitrogen atmosphere without stirring. After concentration, the crude product was purified by chromatography (CH_2Cl_2/MeOH, 30:1) to afford rotaxane **R-2** as a white solid (27 mg, 30%). M.p. 115.9–117.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.00 (s, 2H), 7.63 (m, 2H), 7.34 (m, 2H), 7.29–7.27 (m, 4H), 7.22 (d, J = 8.1 Hz, 12H), 7.07 (d, J = 8.1 Hz, 16H), 6.87 (s, 2H), 6.74 (d, J = 8.3 Hz, 4H), 6.63 (d, J = 8.0 Hz, 4H), 4.58 (m, 4H), 4.19 (t, J = 6.2 Hz, 4H), 4.14 (m, 4H), 4.01 (t, J = 5.7 Hz, 4H), 3.81 (t, J = 5.7 Hz, 4H), 3.77 (m, 4H), 3.73 (m, 4H), 3.67 (m, 4H), 3.55 (t, J = 5.7 Hz, 4H), 3.24 (s, 4H), 3.03 (m, 4H), 2.79 (t, J = 7.0 Hz, 4H), 2.05 (m, 4H), 1.95 (m, 4H), 1.30 ppm (s, 54H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 170.49, 159.60, 156.68, 148.38, 146.33, 144.23, 139.79, 132.34, 130.81, 130.59, 129.15, 126.60, 124.86, 124.13, 122.97, 114.77, 113.09, 107.84, 71.68, 71.22, 70.66, 69.94, 68.74, 65.96, 64.08, 63.14, 62.25, 52.03, 38.87, 34.37, 33.71, 31.65, 31.49, 29.78, 29.45, 28.85, 28.44 ppm; MS (MALDI-TOF): m/z: 2037.4 [M−PF_6^-]$^+$; elemental analysis calcd (%) for $C_{126}H_{158}F_6NO_{14}PS_4$: C 69.30, H 7.29, N 0.64; found: C 69.63 , H 7.62, N 0.66.

[2]Rotaxane R-3: The reaction was carried out as described for the preparation of thread **T-1**. DMPA (1.26 mg, 0.005 mmol) was added to a solution of **9-H**·PF_6 (2.8 mg, 0.008 mmol) and macrocycle M-S[13a] (4.5 mg, 0.010 mmol) in anhydrous CH_2Cl_2 (3 mL). The reaction mixture was irradiated at room temperature for 1 h under a nitrogen atmosphere without stirring. After concentration, the crude product was purified by chromatography (CH_2Cl_2/MeOH, 30:1) to afford rotaxane **R-3** as a white solid (2.5 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.20 (s, 2H), 7.63–7.62 (m, 2H), 7.39–7.37 (m, 6H), 7.16–7.12 (m, 4H), 7.09–7.05 (m, 2H), 6.86 (s, 2H), 4.69–4.66 (m, 4H), 4.14–4.13 (m, 4H), 3.84 (t, J = 6.0 Hz, 4H), 3.76 (m, 4H), 3.71 (m, 4H), 3.60 (m, 4H), 3.05 ppm (t, J = 6.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 146.24, 130.96, 129.69, 129.17, 126.61, 124.98, 108.00, 71.56, 71.29, 70.76, 69.93, 68.84, 52.73, 39.04, 29.44 ppm; MS (MALDI-TOF): m/z: 652.3 [M−PF_6^-]$^+$; elemental analysis calcd (%) for $C_{36}H_{46}F_6NO_6PS_2$: C 54.19, H 5.81, N 1.76; found: C 54.41, H 6.09, N 1.85.

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