How Selective Threading of Amides through Macrocylic Lactam Wheels Leads to Rotaxane Synthesis

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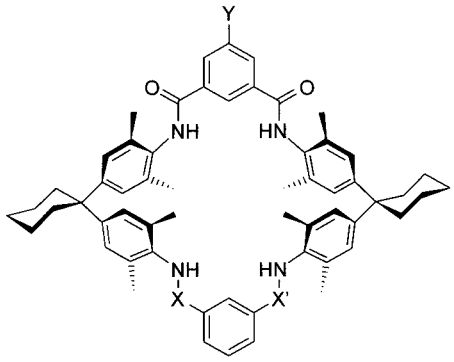
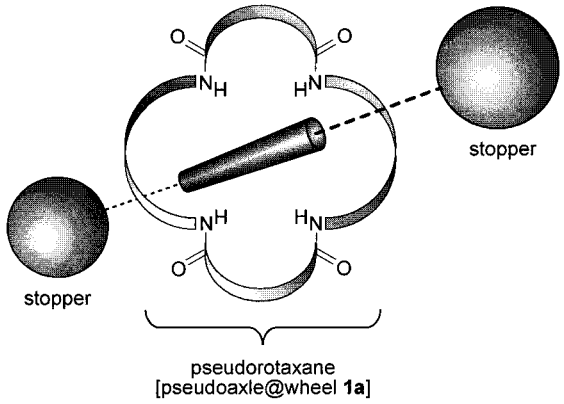
Introduction

Chemistry has often drawn inspiration from molecules with aesthetically appealing architecture. Mechanically interlocked compounds such as rotaxanes, catenanes, and knots are important examples and have grown in importance as a result of the development of template syntheses that significantly improved their yields.[1,2] In particular, rotaxanes are molecular compounds that consist of one or more "wheels" with penetrating "axles", which are mechanically bound together and sterically prevented from dethreading by bulky "stopper groups" at both ends of the axle(s). Semirotaxanes and pseudorotaxanes are analogous to conventional inclusion complexes in that they are not restrained mechanically from dissociation because the axles (in these cases semi- and pseudoaxles, respectively) carry either one stopper only (semiaxle) or no stopper at all (pseudoaxle).[3] Rotaxanes, semirotaxanes, and pseudorotaxanes are conveniently respresented by formulas given as [axle@wheel], [semiaxle@wheel], and [pseudoaxle@wheel], respectively. Semi- and pseudorotaxanes that act as precursors in rotaxane syntheses are called prerotaxanes. In recent years we have reported the synthesis of a series of rotaxanes based on the formation of amide bonds between a diacid chloride axle part and two voluminous amino stoppers in the presence of a macrocylic lactam (e.g., **1**) as the wheel.[1d]

The mechanism of "threading the wheel" is assumed to proceed via a pseudo- or semirotaxane complex. In these complexes the guest is presumably fixed inside the host cavity, orthogonal to the main plane of the macrocycle, by hydrogen bonds between the lactam amide groups and either the acid chloride carbonyl or the amide carbonyl of the pseudo- or semiaxle. Such preorganization of the pseudo- or semiaxles would properly position their reactive groups for further reaction with the stoppers.



1a: X = X' = CO, Y = *t*-Bu
1b: X = SO_2, X' = CO, Y = OCH_3
1c: X = X' = CS, Y = H



pseudorotaxane
[pseudoaxle@wheel **1a**]

Results and Discussion

Host/Guest Studies. A deeper and more detailed insight into the mechanisms of template-assisted synthesis involving macrocyclic lactams could lead to new synthetic strategies. Therefore, we used NMR titrations in CD_2Cl_2 to study the binding properties of the wheels **1**[4] with a range of neutral organic molecules. Studies of complexation of quinone and other cyclic dicarbonyl compounds by such macrocycles has been reported earlier.[5]

The NMR titration results show that tetralactam **1a**[4a] is selective for secondary amides (e.g., **2**, **3a**−**e**, **4a**, and

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(2) For recent accounts on rotaxanes and catenanes with different types of template syntheses, see: (a) Adams, H.; Carver, F. J.; Hunter, C. A. *J. Chem. Soc., Chem. Commun.* **1995**, 809−810. (b) Born, M.; Ritter, H. *Adv. Mater.* **1996**, *8*, 149−151. (c) Hamilton, D. G.; Sanders, J. K. M.; Davies, J. E.; Clegg, W.; Teat, S. J. *Chem. Commun.* **1997**, 897−898. (d) Harada, A.; Li, J.; Kamachi, M. *Chem. Commun.* **1997**, 1413−1414. (e) Herrmann, W.; Schneider, M.; Wenz, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2511−2514. (f) Gong, C.; Gibson, H. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 310−314. (g) Kolchinski, A. G.; Alcock, N. W.; Roesner, R. A.; Busch, D. H. *Chem. Commun.* **1998**, 1437−1438. (h) Fujita, M.; Aoyagi, M.; Ibukuro, F.; Ogura, K.; Yamaguchi, K. *J. Am. Chem. Soc.* **1998**, *120*, 611−612. (i) Leigh, D. A.; Murphy, A.; Smart, J. P.; Deleuze, M. S.; Zerbetto, F. *J. Am. Chem. Soc.* **1998**, *120*, 6458−6467. (j) Armaroli, N.; Diederich, F.; Dietrich-Buchecker, C. O.; Flamigni, L.; Marconi, G.; Nierengarten, J.-F.; Sauvage, J.-P. *Chem. Eur. J.* **1998**, *4*, 406−416. (k) Ashton, P. R.; Ballardini, R.; Balzani, V.; Fyfe, M. C. T.; Gandolfi, M. T.; Martínez-Díaz, M.-V.; Morosini, M.; Schiavo, C.; Shibata, K.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1998**, *4*, 2332−2341. (l) Linke, M.; Chambron, J.-C.; Heitz, V.; Sauvage, J.-P.; Semetey, V. *Chem. Commun.* **1998**, 2469−2470. (m) Hübner, G. M.; Gläser, J.; Seel, C.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 383−386.

(3) See also: Ashton, P. R.; Philp, D.; Spencer, N.; Stoddart, J. F. *J. Chem. Soc., Chem. Commun.* **1991**, 1677−1679.

(4) (a) Vögtle, F.; Händel, M.; Meier, S.; Ottens-Hildebrandt, S.; Ott, F.; Schmidt, T. *Liebigs Ann.* **1995**, 739−743. (b) Ottens-Hildebrandt, S.; Schmidt, T.; Harren, J.; Vögtle, F. *Liebigs Ann.* **1995**, 1855−1860. (c) Braschohs, S.; Ph. D. thesis, University of Bonn, Germany, 1998.

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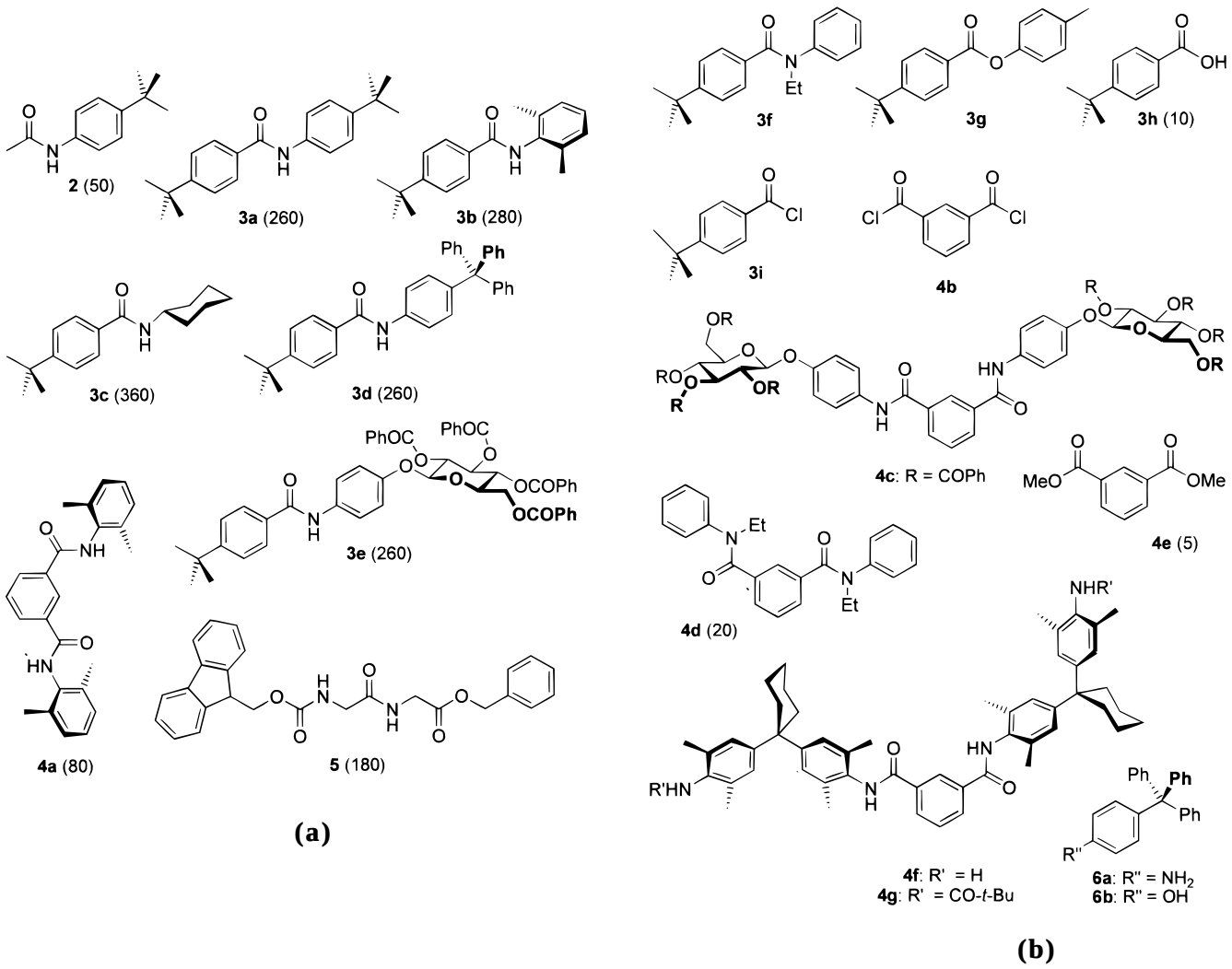


Figure 1. Molecular recognition of neutral organic molecules by wheel **1a** in CD_2Cl_2. (a) Analogous secondary amide axle guests. The association constants (M^{-1}) are given in parentheses. (b) Derivatives that are not significantly bound.

5, see Figure 1a). The slight differences in the association constants of these guests are probably caused by the influence of substituents (aromatic versus aliphatic) on the hydrogen bond donor and acceptor properties (pK_a of NH and pK_b of CO) of the guest. The signals for guest protons in the vicinity of the amide bond undergo stronger complexation-induced shifts than ones further away. This suggests a positioning of the guest that places the amide linkage in the most intense positive region of diamagnetic anisotropy for the arene units of the wheel, while placing other positions along the guest in regions of decreasing diamagnetic anisotropy that scales with the distance from the amide linkage. Such a positioning is consistent with an orthogonal orientation of the guests inside the host cavity.

Carboxylic acid chlorides (**3i**) and diacid chlorides (**4b**) are not significantly bound. This rules out the possibility of pseudorotaxanes, such as [**4b**@**1a**], being the key intermediates in the synthesis; rather it strongly hints at the formation of a reactive semirotaxane complex analogous to that of the type [**3d**@**1a**] as the crucial intermediate in rotaxane generation.

Voluminous groups such as 4-tritylphenyl adjacent to the amide bond as in semiaxles **3d** and **3e** do not influence the binding strength. Hence, steric hindrance from the presence of one stopper does not affect complex formation, i.e., it does not hinder threading of the wheel by the associate axle part of the semiaxle. However, the axle **4c** with two tetrabenzoylglucose stoppers[6] shows no affinity toward the tetralactam. This confirms that the presence of two bulky stoppers such as with **4c** prevent the axle from "slipping" through the macrocycle to form a rotaxane and suggests that as a result no favorable contact between the amide groups of the two molecules is possible.

Upon complexation, the amide proton signals for both the wheel and the guests exhibit downfield shifts typical of hydrogen bonding. X-ray structures of the wheels usually show all four NH protons more or less directed toward the center of the cavity, thus providing multiple docking sites for proton acceptor groups of enclosed solvent molecules.[4c,5,7] In related catenanes, however, one amide bond in each macrocycle is inverted with the carbonyl group pointing inward so that it contacts (i.e.,

(6) Schmidt, T.; Schmieder, R.; Müller, W. M.; Kiupel, B.; Vögtle, F. *Eur. J. Org. Chem.* **1998**, 2003−2007.

(7) (a) Ottens-Hildebrandt, S.; Meier, S.; Nieger, M.; Vögtle, F.; Weber, E. *Supramol. Chem.* **1995**, *5*, 133−138. (b) Vögtle, F.; Dünnwald, T.; Schmidt, T. *Acc. Chem. Res.* **1996**, *29*, 451−460. (c) Fischer, C.; Nieger, M.; Mogck, O.; Böhmer, V.; Ungaro, R.; Vögtle, F. *Eur. J. Org. Chem.* **1998**, 155−161. (d) See also: Clegg, W.; Gimenez-Saiz, C.; Leigh, D. A.; Murphy, A.; Slawin, A. M. Z.; Teat, S. J. *J. Am. Chem. Soc.* **1999**, *121*, 4124−4129.

H-bonds with) an NH proton of the other ring.[2a,8,9] Furthermore, at room temperature there is a weak NOE between the resonances of the lactam NH protons and the isophthaloyl H-3 and H-5 protons, in addition to the expected strong contact between the NH and the H-2 protons. This suggests that in solution there is an equilibrium between the cisoid and transoid rotamers, with the latter being disfavored. All of the lactam spectra retain their general shape and appearance during the titrations, suggesting that the symmetry of the cisoid orientation is maintained. Rapid conformational exchange could, however, explain this. Low-temperature experiments (down to −70 °C) gave no further evidence of any conformational equilibria existing.

In the solid-state, lactams such as **1** can complex esters such as ethyl acetate, as evidenced by several X-ray structures. In these structures the ester carbonyl oxygen and both amide protons of one isophthalic amide moiety in the wheel form bifurcated hydrogen bonds.[7] In solution, however, the binding of esters (**3g** and **4e**), which are weaker hydrogen bond acceptors than amides, is not very pronounced. Likewise, in solution the affinity for binding tertiary amides (**3f** and **4d**) is strongly diminished. Also, amines such as stopper **6a**, alcohols (**6b**), ethers (*m*-dimethoxybenzene), benzoic acids (**3h**), ketones (fluorenone, benzil), phenylisocyanate, and sulfonamides (the analogue of **3a**) are only weakly or negligibly bound.

Monosulfonamide trilactam **1b**, which has also been used as the wheel in rotaxane syntheses,[4b] and the dithiamide macrocycle **1c**[4c] both bind secondary amide pseudoaxles similarly as does the tetralactam **1a**. However, only the isophthalic amide residues of these wheels show the typical upfield shift of NH protons caused by hydrogen bonding. In other words, the phenylsulfonyl and dithiaamide moieties do not seem to act as a binding site for the guests. This is consistent with the previously noted observation that the sulfonamide analogue of **3a** is not bound by the tetralactam **1a**.

Furthermore, open-chain isophthalic diamide **4f**,[9] which also serves as a precursor in the macrocycle synthesis, and the open-chain tetraamide **4g** do not reveal any significant affinity for amide **3c**. Obviously a macrocyclic structure of the host is essential for binding. The reason might be that open-chain isophthalic diamides have a trans conformation of the two amide groups rather than the cis conformation as in the macrocycles, i.e., the NH protons point in opposite directions, which would be unfavorable for the bifurcated hydrogen bonding of a carbonyl oxygen.[10] Because the structurally similar diamide **4a** is relatively well bound as a guest by macrocycle **1a** as a host, it can be assumed that similar pseudorotaxane complexes such as **[4f@1a]** serve as templates for the related catenane synthesis. Because diamides tend to be poorly soluble,[11] especially in nonpolar solvents such as chloroform or dichloromethane, their association constants could not be determined by NMR titration. In fact, the nonplanar diamide **4a** has such a limited solubility in CD_2Cl_2 (ca. 8 mM) that the resulting uncertainty renders the K_a measured by our NMR titration technique merely an approximation. Compounds **4f** and **4g** dissolve even to a lesser extent and thus could not be titrated under the experimental conditions employed.

It has to be pointed out that there is an uncertainty about the hydrogen bonding pattern in the amide complexes. The fact that tertiary amides (which lack an NH proton) are not bound might indicate that in the binding of secondary amides the guest NH proton is directly involved. However, this would imply that one isophthalamide unit of the wheel has to adopt a transoid conformation which is unfavored in the free macrocycle. Also, as a result of steric reasons, only one hydrogen bond could be formed instead of the bifurcated motif seen in X-ray structures as mentioned above. However, NOE experiments give no evidence for the transoid conformation of the macrocycle. Also, the fact that in the rotaxanes described below no downfield shifts of the axle NH protons caused by hydrogen bonding have been observed and this is consistent with the bifurcated motif.[12]

In summary, secondary amides are well bound by macrocycles of appropriate size that feature at least one isophthalic diamide group as the docking site. If the guests carry functional groups for condensation reactions with stopper units and are preorganized in the complexes to give pseudorotaxanes, then synthesis of a great variety of rotaxanes is feasable.[1d]

Rotaxane Syntheses. To test the hypothesis that the crucial intermediate in our rotaxane synthesis is a semirotaxane having the respective semiaxle fixed inside the wheel by hydrogen bonds between the amide groups of the two components, we designed the following experiments as depicted in Scheme 1. The secondary amide **8a**, which is similar to the guest **3d**, and the analogous ester **8b** were synthesized following standard procedures. Both are potential axle precursors because they are stoppered with a trityl group on one end and carry an anilinic NH_2 group on the other; the NH_2 group can react with a second stopper containing a benzoyl chloride group (**9**). Rotaxanes should be possible only if wheel **1a** and the semiaxles form appropriately preorganized inclusion complexes. To stabilize the prerotaxane complexes [**8**@**1a**] we worked at low temperature (−5 °C) and as high a concentration as possible (4 mM; about the limit of solubility for **1a**). These conditions shift the association equilibrium toward complexation. Indeed, rotaxane **10a** was formed as expected and with the high yield of 69%, a result that strongly supports our mechanistic model. In contrast, only 4% of the analogous ester rotaxane **10b** was obtained; this is consistent with a weak but obviously not negligible complexation of esters by **1a** in solution.

It was possible to synthesize several rotaxanes with aliphatic axle middle parts by this synthetic approach. Therefore any contribution from hydrophobic arene−arene interactions to the mechanism of preorganiztion cannot be very pronounced. In particular, aliphatic diacid chlorides were reacted with 2 equiv of stopper **6a** in the presence of wheel **1a**. The yields for the rotaxanes **11**−

(8) (a) Ottens-Hildebrandt, S.; Nieger, M.; Rissanen, K.; Rouvinen, J.; Meier, S.; Harder, G.; Vögtle, F. *J. Chem. Soc., Chem. Commun.* **1995**, 777−778. (b) A rotaxane was reported where one amide bond also seems to be inverted: Leigh, D. A.; Murphy, A.; Smart, J. P.; Slawin, A. M. Z. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 752−756.

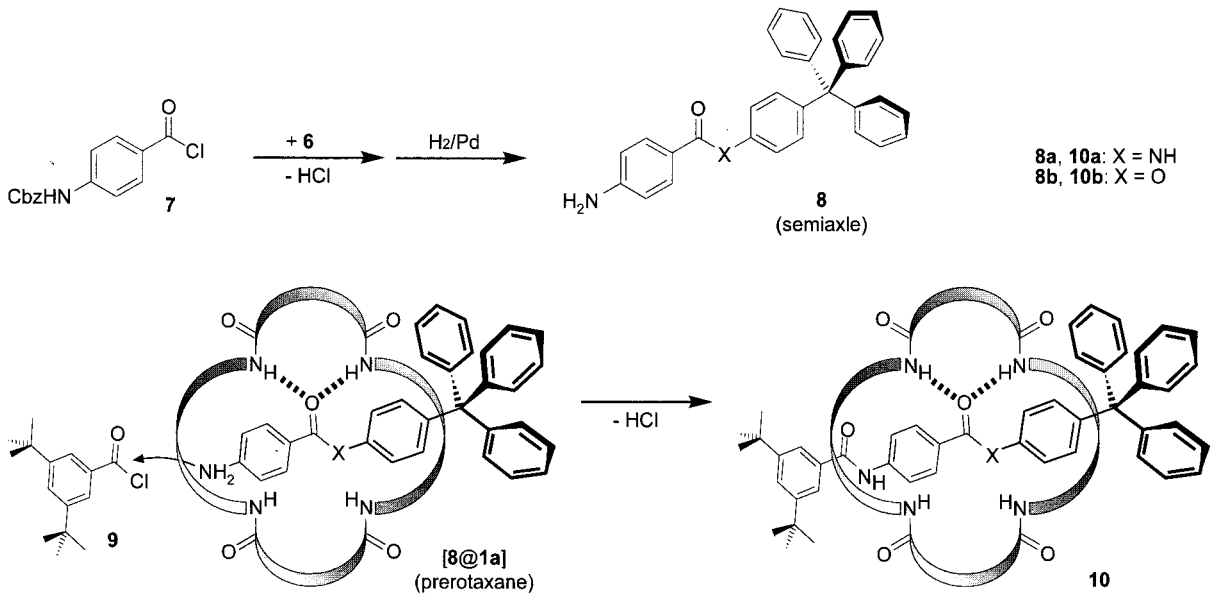
(9) Hunter, C. A. *J. Am. Chem. Soc.* **1992**, *114*, 5303−5311.

(10) (a) Carver, F. J.; Hunter, C. A.; Shannon, R. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1277−1280. See also ref 5b and: Adams, H.; Harris, K. D. M.; Hembury, G. A.; Hunter, C. A.; Livingstone, D.; McCabe, J. F. *Chem. Commun.* **1996**, 2531−2532.

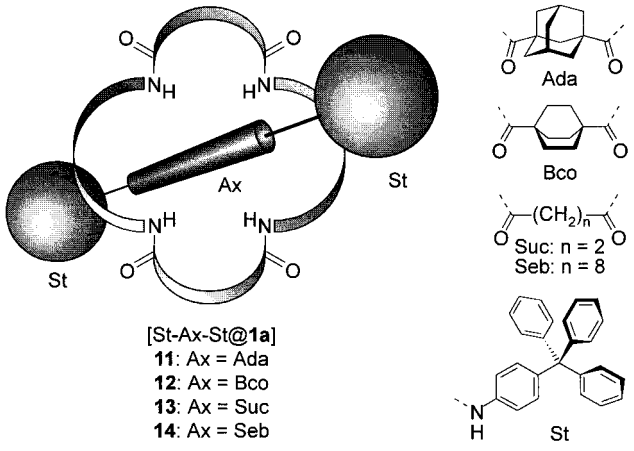
(11) See also: Eblinger, F.; Schneider, H.-J. *Angew. Chem., Int. Ed.* **1998**, *37*, 826−829.

(12) After submission of this paper we were able to determine the X-ray structure of a related rotaxane. It indeed shows the bifurcated hydrogen bonding pattern between the NH protons of one isophthalamide group of wheel **1b** and an amide oxygen of the axle. Reuer, C.; Nieger, M.; Vögtle, F., unpublished results.

Scheme 1



13 from adamantane-1,3-dicarbonyl chloride, bicyclo-[2.2.2]octane-1,4-dicarbonyl chloride, and succinyl chloride were 44%, 25%, and 23%, respectively. These yields are lower than for the case of **10a** most likely because two bonds have to be formed instead of just one. Additionally, the synthesis of rotaxane **14** from the *N*-hydroxysuccinimide ester of sebacinic acid (instead of its diacid chloride) gave a yield of 11%. This further indicates that recognition and binding of the acid chloride group is not crucial for rotaxane formation. It also demonstrates that active esters are useful alternatives to acid chlorides in the synthesis of rotaxanes with amide axles.



Chemical Shifts Induced by the Mechanical Bonding in Rotaxanes. All of the newly synthesized rotaxanes exhibit the typical interlocking-induced shifts of signals in the NMR spectra. Signals of protons in the central parts of the axles undergo the strongest upfield shifts because they are positioned deeply inside the negative region of the anisotropic fields of the aromatic units of the cyclophane wheel. The aromatic protons of the 4-aminobenzoyl unit shift by 1.9 and 1.8 ppm upfield in case of rotaxane **10a** and 1.5 and 1.3 ppm in case of **10b**. The further the protons are away from the center of the complex, the less pronounced are the effects. For example, the $\Delta\delta$ values for the H-2 and H-6 protons of the 3,5-di-*tert*-butylbenzoyl stopper are only 0.3 ppm for **10a** and 0.35 ppm for **10b**. The amide proton signals of the wheels, however, shift downfield, obviously as a result of hydrogen bonding with the carbonyl oxygens of the axles. The same is not true, however, for the amide protons of the axles. This stands in contrast to the downfield shifts of the NH protons of the guests in the titrations, a fact that is not easy to explain. In **10a** the signals of the two pairs of lactam NH protons shift by 1.05 ppm on average. In **10b**, which has a monoamide−monoester axle, the effect is only about half as large at 0.58 ppm. Here only one isophthalamide unit at a time can interact with the amide group of the axle. Hydrogen bonding to the ester group seems much less effective, which correlates with the weak binding of esters as guests by the tetralactam host **1a**.

Low solubility of the rotaxanes **11**−**14** with aliphatic axle middle parts (and even lower solubility of the corresponding free axles) prevented the use of pure $CDCl_3$ as a solvent; mixtures with CD_3OD or DMSO-d_6 were required. Because these media weaken or suppress the formation of hydrogen bonds, the induced changes in the chemical shifts of the wheel amide protons are far less pronounced for these samples. Line-broadening of the signals of the adamantane residue and overlap with signals of the wheel in rotaxane **11** make it difficult to assign and quantify the shifts. The signal of the adamantane CH_2 group not neighboring the carbonyls (CH_2-10) shifts 1.4 ppm and the axle NH signal 0.5 ppm upfield in DMSO-d_6. Similarly, in **12** the bicyclo[2.2.2]octane signal shifts 0.8 ppm and the axle NH proton 0.4 ppm in DMSO-d_6/$CDCl_3$ (2:1). In the case of rotaxanes **13** and **14**, the shorter succinamide axle in **13** leads to somewhat larger upfield shifts. The NH signals of the axle shift 1.3 ppm in **13**, as compared to 0.4 ppm in **14**; the signals due to the methylene groups shift 0.75 ppm for **13**, as compared to 0.4−0.6 ppm for **14** in DMSO-d_6/$CDCl_3$ (1:1).

Conclusions

We recently published a study of the anion-binding abilities of macrocyclic tetralactams.[2m] We now report that in binding neutral molecules in nonpolar solvents

these host molecules are rather selective for secondary amides. Both types of molecular recognition (i.e., of anions and of secondary amides) have been successfully utilized for the template-assisted synthesis of mechanically interlocked molecules. We are currently investigating different linking reaction types as new strategies for synthesizing these intriguing compounds and possibly extending them to more sophisticated structures.

Experimental Section

Materials. 4-Tritylaniline (Aldrich), 4-tritylphenol (Lancaster), 3,5-di-*tert*-butylbenzoic acid (Lancaster), 4-aminobenzoic acid (Merck), adamantane-1,3-dicarboxylic acid (Fluka), succinyl dichloride (Merck), sebacoyl dichloride (Merck), and all other chemicals were of the best commercial quality available and used as received. The macrocycles[4] and bicyclo[2.2.2]octane-1,4-dicarboxylic acid[13] were prepared as previously reported. Acid chlorides and guest compounds, if not commercial, were synthesized and purified by standard procedures.

Microanalyses were performed by the analytical facility of the Kekulé-Institut für Organische Chemie und Biochemie of the University of Bonn. Solvent retention in the analytical samples was verified by NMR. One equivalent of ethyl acetate is routinely found after column chromatography of samples of tetralactam wheels and rotaxanes of this type.[7]

Assignments of the signals of NH protons in the ^{1}H NMR spectra were made by deuterium exchange experiments and the pronounced solvent dependency of the chemical shifts.

Determination of Binding Constants. Titrations were performed by adding aliquots (usually 25, 30, 35, 40, 50, 70, 100, and 150 μL) of a solution of the guest to a solution (500 μL) of the macrocycle, both in CD_2Cl_2. Typical concentrations were 30 mM of guest and 4 mM of host, but higher concentrations were used in cases of weak binding. The complexation of the guests was monitored by measuring the complexation-induced shifts of the signals for the NH protons, the H-2 protons of the isophthalic acid residues, and the arylic methyl protons of the macrocycles. Standard nonlinear curve fitting of the shift values gave the association constants (K_a), the average of which is given in each case.[14] The experimental data, including Job-plots,[15] were consistent with 1:1 stoichiometry for all complexes.

Z-Protected Semiaxles Z-8a and Z-8b. A solution of 360 mg (1.13 mmol) of *N*-benzyloxycarbonyl-4-aminobenzoyl chloride[16] in 50 mL of CH_2Cl_2 is added dropwise during 2 h to a solution of 8 drops of triethylamine and 379 mg (1.13 mmol) of 4-tritylaniline (**6a**) or 380 mg (1.13 mmol) of 4-tritylphenol (**6b**) in 50 mL of CH_2Cl_2. After 2 h of additional stirring the solvent is evaporated, and the residue is purified by column chromatography [SiO_2, CH_2Cl_2].

(4-Benzyloxycarbonylaminobenz)-4-tritylanilide (Z-8a). Colorless solid. Yield: 520 mg (79%). Mp: 96 °C. R_f 0.14 (CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.21 (2H, s), 6.91 (1H, s, NH), 7.15−7.40 (22H, m), 7.49 (2H, d, J = 8.6 Hz), 7.50 (2H, d, J = 8.6 Hz), 7.75 (1H, s, NH), 7.79 (2H, d, J = 8.6 Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$/CD_3OD 5:1) δ 64.38 (C_q), 66.78 (CH_2), 117.82 (CH), 119.31 (CH), 125.69 (CH), 127.25 (CH), 127.87 (CH), 128.09 (CH), 128.18 (CH), 128.35 (CH), 128.87 (C_q), 130.86 (CH), 131.39 (CH), 135.80 (C_q), 138.88 (C_q), 141.57 (C_q), 142.66 (C_q), 146.56 (C_q), 153.65 (C_q), 166.21 (C_q). FABMS (3-nitrobenzyl alcohol): 589.2 $(M + H)^+$. Anal. Calcd for $C_{40}H_{32}N_2O_3 \cdot 0.5H_2O$: C, 80.38; H, 5.56; N, 4.67. Found: C, 80.57; H, 5.42; N, 4.55.

4-Tritylphenyl 4-(Benzyloxycarbonylamino)benzoate (Z-8b). Colorless solid. Yield: 379 mg (58%). Mp: 200 °C. R_f 0.66 (CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.24 (2H, s), 7.01 (1H, s, NH), 7.10 (2H, d, J = 8.6 Hz), 7.15−7.40 (22H, m), 7.52 (2H, d, J = 8.6 Hz), 8.13 (2H, d, J = 8.6 Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 64.59 (C_q), 67.39 (CH_2), 117.63 (CH), 120.53 (CH), 124.08 (C_q), 125.98 (CH), 127.52 (CH), 128.39 (CH), 128.53 (CH), 128.66 (CH), 131.08 (CH), 131.55 (CH), 132.13 (CH), 135.57 (C_q), 142.69 (C_q), 144.30 (C_q), 146.57 (C_q), 148.84 (C_q), 152.78 (C_q), 166.64 (C_q). FABMS (3-nitrobenzyl alcohol): 590.3 $(M + H)^+$. Anal. Calcd for $C_{40}H_{31}NO_4$: C, 81.47; H, 5.30; N, 2.38. Found: C, 81.30; H, 5.25; N, 2.32.

Synthesis of Semiaxles 8a and 8b. A 0.6 mmol portion of Z-**8a** or Z-**8b** and 10 mg of Pd/C in 40 mL of ethanol are shaken under 3 bar H_2 atmosphere for 4 h. After filtration the solvent is evaporated, and the residue is purified by column chromatography [SiO_2, CH_2Cl_2].

(4-Aminobenz)-*p*-tritylanilide (8a). Colorless solid. Yield: 265 mg (91%). Mp: 232 °C. R_f 0.11 (CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.07 (2H, s, NH_2), 6.69 (2H, d, J = 8.6 Hz), 7.20 (2H, d, J = 8.6 Hz), 7.15−7.30 (15H, m), 7.48 (2H, d, J = 8.6 Hz), 7.65 (1H, s, NH), 7.68 (2H, d, J = 8.6 Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$/CD_3OD 5:1) δ 64.37 (C_q), 113.91 (CH), 119.18 (CH), 125.69 (CH), 128.85 (CH), 130.86 (CH), 131.37 (CH), 136.01 (C_q), 136.09 (C_q), 142.36 (C_q), 146.59 (C_q), 150.18 (C_q), 166.41 (CO). FABMS (3-nitrobenzyl alcohol): 455.3 $(M + H)^+$. Anal. Calcd for $C_{32}H_{26}N_2O \cdot 0.5H_2O$: C, 83.09; H, 6.05 N, 5.67. Found: C, 83.39; H, 5.73 N, 5.91.

***p*-Tritylphenyl 4-Aminobenzoate (8b).** Colorless solid. Yield: 256 mg (88%). Mp: 245 °C. R_f 0.41 (CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$) δ 4.1 (2H, br, NH), 6.67 and 7.98 (4H, AA′BB′, ^3J = 8.5 Hz), 7.08 (2H, half of AA′BB′, ^3J = 8.7 Hz), 7.15−7.25 (17H, m). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 64.57 (C_q), 114.12 (CH), 120.66 (CH), 125.95 (CH), 127.50 (CH), 127.57 (C_q), 131.09 (CH), 132.06 (CH), 132.28 (CH), 143.99 (C_q), 146.60 (C_q), 146.63 (C_q), 149.05 (C_q), 165.01 (CO). FABMS (3-nitrobenzyl alcohol): 456.2 $(M + H)^+$. Anal. Calcd for $C_{32}H_{25}NO_2$: C, 84.37; H, 5.53 N, 3.07. Found: C, 84.36; H, 5.65 N, 2.93.

Synthesis of Rotaxanes 10a and 10b. A 384 mg (0.4 mmol) portion of tetralactam **1a**, 0.4 mmol of semiaxle **8a** or **8b**, and 12 drops of triethylamine are dissolved in 100 mL of CH_2Cl_2 and cooled to −5 °C. A solution of 102 mg (0.4 mmol) of 3,5-di-*tert*-butylbenzoyl chloride **9** in 100 mL of CH_2Cl_2 is added dropwise during 4 h. After 2 h of additional stirring the solvent is evaporated, and the residue is purified by column chromatography [SiO_2, CH_2Cl_2/ethyl acetate (25:1)] to yield the rotaxanes and free axles. **10a.** Colorless solid. Yield: 449 mg (69%). Mp: >320 °C. R_f 0.43 (CH_2Cl_2/ethyl acetate 25:1). ^{1}H NMR (250 MHz, $CDCl_3$/CD_3OD 5:1) δ 1.23 (18H, s), 1.41 (9H, s), 1.50 (4H, br), 1.61 (8H, br), 1.84 (12H, s), 1.85 (12H, s), 2.22 (4H, br), 2.28 (4H, br), 6.01 and 6.12 (4H, AA′BB′, ^3J = 8.4 Hz), 6.95 (4H, s), 6.96 (4H, s), 7.15−7.35 (20H, m), 7.49 (2H, d, J = 1.6 Hz), 7.59 (1H, t, J = 1.6 Hz), 7.67 (1H, t, J = 7.8 Hz), 8.11 (2H, d, J = 7.8 Hz), 8.17 (2H, s), 8.25 (1H, s), 8.40 (1H, s), 8.51 (2H, s, NH), 8.55 (2H, s, NH). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 18.53 (CH_3), 18.59 (CH_3), 22.86 (CH_2), 22.99 (CH_2), 26.26 (CH_2), 31.24 (CH_3), 34.96 (C_q), 35.22 (C_q), 35.64 (CH_2), 36.58 (CH_2), 45.32 (C_q), 64.63 (C_q), 118.45 (CH), 121.62 (CH), 124.08 (CH), 124.22 (CH), 125.88 (CH), 126.13 (CH), 126.44 (CH), 126.70 (CH), 126.90 (CH), 127.22 (CH), 127.44 (CH), 127.65 (CH), 128.57 (CH), 129.73 (CH), 130.97 (CH), 131.34 (C_q), 131.46 (CH), 131.62 (C_q), 131.75 (C_q), 131.89 (C_q), 132.18 (CH), 134.46 (C_q), 134.70 (C_q), 134.77 (C_q), 135.07 (C_q), 135.16 (C_q), 139.57 (C_q), 144.46 (C_q), 146.37 (C_q), 148.37 (C_q), 148.51 (C_q), 151.85 (C_q), 153.43 (C_q), 165.95 (CO), 166.59 (CO), 167.16 (CO), 169.17 (CO). MALDI-TOFMS (2,5-dihydroxybenzoic acid): 1654.7 $(M + Na)^+$, 1671.7 $(M + K)^+$. Anal. Calcd for $C_{111}H_{118}N_6O_6 \cdot 2H_2O \cdot C_4H_8O_2$: C, 78.65; H, 7.46; N, 4.79. Found: C, 78.86; H, 7.50; N, 4.81.

4-(3,5-Di-*tert*-butylbenzamido)benz-(4-tritylanilide) (free axle of 10a). Colorless solid. Yield: 40 mg (15%). Mp: 198 °C. R_f 0.31 (CH_2Cl_2/ethyl acetate 25:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.36 (9H, s), 7.15−7.30 (19H, m), 7.52 (2H, half of AA′BB′, ^3J = 8.8 Hz), 7.63 (1H, t, J = 1.7 Hz), 7.66 (2H, d, J = 1.7 Hz), 7.78 (1H, s, NH), 7.78 and 7.85 (4H, AA′BB′, ^3J = 8.7 Hz), 7.90 (1H, s, NH).^{13}C NMR (62.9 MHz, $CDCl_3$) δ 31.09 (CH_3), 34.82 (C_q), 64.42 (C_q), 119.29 (CH), 120.17 (CH), 121.44 (CH), 125.72 (CH), 126.14 (CH), 127.29 (CH), 128.07 (CH), 130.24 (C_q), 130.90 (CH), 131.44 (CH), 133.85 (C_q), 135.95 (C_q), 141.36 (C_q), 142.69 (C_q), 146.59 (C_q), 151.24 (C_q), 166.31 (CO), 167.99 (CO). MALDI-TOFMS (2,5-dihydroxybenzoic acid): 671.9 $(M + H)^+$, 693.9 (M

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+ Na)$^+$, 709.8 (M + K)$^+$. Anal. Calcd for $C_{47}H_{46}N_2O_2 \cdot 2H_2O$: C, 79.86; H, 7.13; N, 3.96. Found: C, 80.29; H, 6.87; N, 3.91.

10b. Colorless solid. Yield: 24 mg (3.6%). Mp: 285 °C. R_f 0.31 (CH_2Cl_2/ethyl acetate 25:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.23 (18H, s), 1.38 (9H, s), 1.50 (4H, br), 1.60 (8H, br), 1.88 (24H, s), 2.24 (8H, br), 6.31 (2H, d, J = 8.3 Hz), 6.77 (2H, d, J = 8.6 Hz), 6.85−6.95 (12H, m), 7.15−7.30 (17H, m), 7.45 (2H, s), 7.61 (1H, s), 7.61 (1H, t, J = 7.7 Hz), 7.73 (4H, s, NH), 8.02 (1H, s), 8.12 (2H, d, J = 7.7 Hz), 8.18 (3H, s). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 18.56 (CH_3), 18.59 (CH_3), 22.96 (CH_2), 26.28 (CH_2), 31.22 (CH_3), 31.33 (CH_3), 34.94 (C_q), 35.27 (C_q), 35.65 (CH_2), 36.21 (CH_2), 45.35 (C_q), 64.56 (C_q), 119.50 (CH), 121.16 (CH), 122.54 (CH), 122.97 (CH), 125.64 (CH), 125.83 (C_q), 125.98 (CH), 126.19 (CH), 126.76 (CH), 126.85 (CH), 127.24 (CH), 127.52 (CH), 127.65 (CH), 128.76 (CH), 129.80 (CH), 130.95 (CH), 131.07 (CH), 131.19 (C_q), 131.27 (C_q), 131.52 (CH), 131.85 (C_q), 132.18 (CH), 134.55 (C_q), 134.83 (C_q), 134.94 (C_q), 141.69 (C_q), 145.05 (C_q), 146.32 (C_q), 146.56 (C_q), 148.20 (C_q), 148.45 (C_q), 151.87 (C_q), 153.76 (C_q), 165.58 (CO), 166.08 (CO), 166.69 (CO), 168.30 (CO). MALDI-TOFMS (2,5-dihydroxybenzoic acid): 1654.2 (M + Na)$^+$. Anal. Calcd for $C_{111}H_{117}N_5O_7 \cdot 4H_2O \cdot C_4H_8O_2$: C, 77.02; H, 7.47; N, 3.91. Found: C, 77.16; H, 7.30; N, 3.67.

4-Tritylphenyl 4-(3,5-Di-*tert*-butylbenzamido)benzoate (free axle of 10b). Colorless solid. Yield: 147 mg (55%). Mp: 250 °C. R_f 0.91 (CH_2Cl_2/ethyl acetate 25:1). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.36 (9H, s), 7.10 and 7.27 (4H, AA′BB′, ^3J = 8.8 Hz), 7.15−7.25 (15H, m), 7.64 (1H, t, J = 1.8 Hz), 7.70 (2H, d, J = 1.8 Hz), 7.81 and 8.18 (4H, AA′BB′, ^3J = 8.9 Hz), 8.15 (1H, br, NH).^{13}C NMR (62.9 MHz, $CDCl_3$) δ 31.29 (CH_3), 34.96 (C_q), 64.54 (C_q), 119.43 (CH), 120.49 (CH), 121.32 (CH), 124.64 (C_q), 125.94 (CH), 126.39 (CH), 127.49 (CH), 131.02 (CH), 131.35 (CH), 132.10 (CH), 134.14 (C_q), 143.11 (C_q), 144.33 (C_q), 146.51 (C_q), 148.76 (C_q), 151.55 (C_q), 164.70 (CO), 176.21 (CO). MALDI-TOFMS (2,5-dihydroxybenzoic acid): 672.8 (M + H)$^+$, 694.8 (M + Na)$^+$. Anal. Calcd for $C_{47}H_{45}NO_3$: C, 84.02; H, 6.75; N, 2.08. Found: C, 83.56; H, 6.73; N, 1.97.

Synthesis of Rotaxanes 11 and 12. A 384 mg (0.4 mmol) portion of tetralactam **1a** and 0.4 mmol of adamantane-1,3-dicarbonyl chloride or bicyclo[2.2.2]octane-1,4-dicarbonyl chloride are dissolved in 100 mL of CH_2Cl_2 and cooled to −5 °C. A solution of 268 mg (0.8 mmol) of 4-tritylaniline (**6a**) and 12 drops of triethylamine in 100 mL of CH_2Cl_2 is added dropwise during 4 h. After 2 h of additional stirring the solvent is evaporated, and the residue is purified by column chromatography [SiO_2, CH_2Cl_2/ethyl acetate (25:1)] to yield the rotaxanes and free axles.

11. Colorless solid. Yield: 320 mg (44%). Mp: 260 °C. R_f 0.32 (CH_2Cl_2/ethyl acetate 25:1). ^{1}H NMR (250 MHz, DMSO-d_6) δ 0.25 (2H, br), 1.2 (2H, br), 1.3 (8H, br), 1.36 (9H, s), 1.4−1.6 (14H, br), 1.91 (12H, s), 1.95 (12H, s), 2.29 (8H, br), 6.95−7.35 (46H, m), 7.67 (1H, t, J = 7.7 Hz), 8.08 (4H, s+d, overlapped), 8.53 (1H, s), 8.62 (1H, s), 8.71 (2H, s, NH), 9.18 (2H, br, NH), 9.30 (2H, br, NH). ^{13}C NMR (62.9 MHz, $CDCl_3$/CD_3OD 5:1) δ 18.40 (CH_3), 18.48 (CH_3), 22.59 (CH_2), 26.07 (CH_2), 27.66 (CH), 30.84 (CH_3), 34.78 (CH_2), 34.94 (C_q), 36.99 (CH_2), 38.78 (CH_2), 41.02 (C_q), 44.64 (C_q), 64.31 (C_q), 120.08 (CH), 125.65 (CH), 125.72 (CH), 127.25 (CH), 128.45 (CH), 129.15 (CH), 130.74 (CH), 130.94 (CH), 130.98 (CH), 131.01 (CH), 133.42 (C), 133.91 (C_q), 134.76 (C_q), 134.87 (C_q), 142.97 (C_q), 146.39 (C_q), 147.42 (C_q), 147.61 (C_q), 152.95 (C_q), 166.06 (CO), 166.27 (CO), 176.81 (CO). MALDI-TOFMS (2,5-dihydroxybenzoic acid): 1821.9 (M + H)$^+$, 1843.9 (M + Na)$^+$. Anal. Calcd for $C_{126}H_{126}N_6O_6 \cdot H_2O \cdot C_4H_8O_2$: C, 81.05; H, 7.12; N, 4.36. Found: C, 80.79; H, 7.01; N, 4.42.

***N,N′*-(4-Tritylphenyl)adamantane-1,3-dicarboxylamide (free axle of 11).** Colorless solid. Yield: 42 mg (12%). Mp: >320 °C. R_f 0.81 (CH_2Cl_2/ethyl acetate 25:1). ^{1}H NMR (250 MHz, DMSO-d_6) δ 1.67 (2H, br), 1.87 (8H, br), 2.04 (2H, br), 2.16 (2H, br), 7.02 and 7.55 (8H, AA′BB′), 7.1−7.3 (30H, m), 9.23 (2H, s, NH). MALDI-TOFMS (2,5-dihydroxybenzoic acid): 859.4 (M + H)$^+$, 881.4 (M + Na)$^+$. Anal. Calcd for $C_{62}H_{54}N_2O_2 \cdot H_2O$: C, 84.90; H, 6.43; N, 3.19. Found: C, 84.90; H, 6.14; N, 3.06.

12. Colorless solid. Yield: 180 mg (25%). Mp: >320 °C. R_f 0.44 (CH_2Cl_2/ethyl acetate 25:1). ^{1}H NMR (250 MHz, DMSO-d_6/$CDCl_3$ 2:1) δ 1.01 (12H, s), 1.36 (9H, s), 1.46 (4H, br), 1.53 (8H, br), 1.92 (24H, s), 2.30 (8H, br), 6.98 (16H, br), 7.1−7.3 (30H, m), 7.69 (1H, t, J = 7.7 Hz), 8.07 (2H, d, J = 7.7 Hz), 8.09 (2H, s), 8.46 (1H, s), 8.57 (1H, s), 8.60 (2H, s, NH), 9.06 (2H, s, NH), 9.19 (2H, s, NH). ^{13}C NMR (62.9 MHz, DMSO-d_6) δ 18.70 (CH_3), 22.64 (CH_2), 25.88 (CH_2), 27.00 (CH_2), 29.03 (CH_2), 31.02 (CH_3), 34.59 (CH_2), 34.86 (C_q), 38.56 (C_q), 64.08 (C_q), 120.98 (CH), 121.01 (CH), 125.49 (CH), 125.97 (CH), 127.70 (CH), 129.39 (CH), 130.39 (CH), 130.84 (CH), 132.10 (C_q), 134.16 (C_q), 134.45 (C_q), 135.66 (C_q), 135.75 (C_q), 142.11 (C_q), 146.45 (C_q), 152.31 (C_q), 164.85 (CO), 176.86 (CO). MALDI-TOFMS (2,5-dihydroxybenzoic acid): 1794.6 (M + H)$^+$, 1816.6 (M + Na)$^+$, 1833.7 (M + K)$^+$. Anal. Calcd for $C_{124}H_{124}N_6O_6 \cdot 5H_2O \cdot C_4H_8O_2$: C, 77.94; H, 7.26; N, 4.26. Found: C, 77.50; H, 7.02; N, 4.14.

***N,N′*-(4-Tritylphenyl)bicyclo[2.2.2]octane-1,4-dicarboxylamide (free axle of 12).** Colorless solid. Yield: 52 mg (15%). Mp: >320 °C. R_f 0.84 (CH_2Cl_2/ethyl acetate 25:1). ^{1}H NMR (250 MHz, DMSO-d_6/$CDCl_3$ 2:1) δ 1.82 (12H, s), 7.02 and 7.50 (8H, AA′BB′, J = 8.1 Hz), 7.1−7.25 (30H, m), 9.04 (2H, br, NH). MALDI-TOFMS (2,5-dihydroxybenzoic acid): 833.7 (M + H)$^+$, 855.5 (M + Na)$^+$, 872.5 (M + K)$^+$. Anal. Calcd for $C_{60}H_{52}N_2O_2 \cdot 3H_2O$: C, 81.24; H, 6.59; N, 3.16. Found: C, 80.88; H, 6.32; N, 2.99.

Synthesis of Rotaxane 13. A 384 mg (0.4 mmol) portion of tetralactam **1a** and 62 mg (0.4 mmol) of succinyl dichloride are dissolved in 200 mL of CH_2Cl_2 and cooled to −5 °C. A solution of 268 mg (0.8 mmol) of 4-tritylaniline (**6a**) and 12 drops of triethylamine in 200 mL of CH_2Cl_2 is added dropwise during 4 h. After 24 h of additional stirring the solvent is evaporated, and the residue is purified by column chromatography [SiO_2, CH_2Cl_2/ethyl acetate (15:1)] to yield the rotaxane and the free axle.

13. Colorless solid. Yield: 157 mg (23%). Mp: >340 °C. R_f 0.19 (CH_2Cl_2/ethyl acetate 20:1). ^{1}H NMR (250 MHz, $CDCl_3$/DMSO-d_6 1:1) δ 1.27 (9H, s), 1.49 (4H, br), 1.57 (8H, br), 1.83 and 1.84 (28H, 2s + br), 2.28 (8H, br), 6.77 and 6.83 (8H, AA′BB′, ^3J = 8.9 Hz), 6.88 (8H, s), 7.05−7.2 (30H, m), 7.52 (1H, t, J = 7.7 Hz), 8.00 (2H, d, J = 7.7 Hz), 8.06 (2H, s), 8.21 (1H, s), 8.32 (2H, s, NH), 8.40 (1H, s), 9.16 (2H, s, NH), 9.20 (2H, s, NH). ^{13}C NMR (62.9 MHz, DMSO-d_6/$CDCl_3$ 2:1) δ 18.19 (CH_3), 18.23 (CH_3), 22.53 (CH_2), 25.83 (CH_2), 30.19 (CH_2), 30.86 (CH_3), 34.64 (CH_2), 44.41 (C_q), 63.85 (C_q), 118.41 (CH), 121.74 (CH), 125.37 (CH), 125.63 (CH), 127.22 (CH), 128.70 (CH), 130.13 (CH), 130.33 (CH), 130.52 (CH), 132.07 (C_q), 132.19 (C_q), 134.00 (C_q), 134.24 (C_q), 134.75 (C_q), 135.75 (C_q), 141.15 (C_q), 146.21 (C_q), 146.84 (C_q), 147.00 (C_q), 151.76 (C_q), 164.55 (CO), 164.92 (CO), 170.23 (CO). MALDI-TOFMS (2,5-dihydroxybenzoic acid): 1736.6 (M + Na)$^+$. FABMS (3-nitrobenzyl alcohol): 1713.0 (M + H)$^+$. Anal. Calcd for $C_{118}H_{116}N_6O_6 \cdot H_2O \cdot C_4H_8O_2$: C, 80.50; H, 6.98; N, 4.62. Found: C, 80.29; H, 6.80; N, 4.76.

***N,N′*-(4-Tritylphenyl)succinamide (free axle of 13).** Colorless solid. Yield: 96 mg (32%). Mp: 273 °C. R_f 0.33 (CH_2Cl_2/ethyl acetate 20:1). ^{1}H NMR (250 MHz, $CDCl_3$/DMSO-d_6 1:1) δ 2.60 (4H, s), 7.00 and 7.43 (8H, AA′BB′, ^3J = 8.7 Hz), 7.1−7.2 (15H, m), 9.82 (2H, s, NH). FABMS (3-nitrobenzyl alcohol): 753.4 (M + H)$^+$. Anal. Calcd for $C_{54}H_{44}N_2O_2 \cdot 0.5H_2O$: C, 85.12; H, 5.95; N, 3.68. Found: C, 85.16; H, 5.89; N, 3.80.

Synthesis of Rotaxane 14. A mixture of 384 mg (0.4 mmol) of tetralactam **1a** and 159 mg (0.4 mmol) of di-*N*-succinimidyl sebacinate[17] in 100 mL of CH_2Cl_2 is added dropwise during 4 h to a refluxing solution of 268 mg (0.8 mmol) of 4-tritylaniline (**6a**) and 98 mg (0.8 mmol) of *N*,*N*-dimethylaminopyridin in 100 mL of CH_2Cl_2. After 24 h of additional stirring at room temperature the solvent is evaporated, and the residue is purified by column chromatography [SiO_2, CH_2Cl_2/ethyl acetate (20:1)] to yield the rotaxane and the free axle.

14. Colorless solid. Yield: 80 mg (11%). Mp: 312 °C. R_f 0.35 (CH_2Cl_2/ethyl acetate 20:1).^{1}H NMR (250 MHz, DMSO-d_6) δ 0.76 (4H, br), 1.09 (4H, br), 1.32 (9H, s), 1.46 (4H, br), 1.55 (8H, br), 1.69 (4H, br t), 1.95 (24H, s), 2.29 (8H, br), 6.9−7.3 (46H, m), 7.61 (1H, t, J = 7.7 Hz), 8.01 (2H, d, J = 7.7 Hz), 8.04 (2H, s), 8.37 (1H, s), 8.50 (1H, s), 9.16 (2H, s, NH), 9.21 (2H, s, NH), 9.41 (2H, s, NH). ^{13}C NMR (62.9 MHz, DMSO-d_6, 50 °C) δ 18.27 (CH_3), 22.54 (CH_2), 24.38 (CH_2), 25.76 (CH_2), 28.32 (CH_2), 30.83 (CH_3), 34.62 (CH_2), 35.51 (CH_2), 44.41 (C_q), 63.87 (C_q), 118.69 (CH), 125.44 (CH), 125.72 (CH), 126.92 (CH), 127.39 (CH), 130.23 (CH), 130.41 (CH), 132.13 (C_q), 134.23 (C_q), 134.29 (C_q), 134.36 (C_q), 134.54 (C_q), 136.27 (C_q), 141.01 (C_q), 146.28 (C_q),

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146.62 (C_q), 151.95 (C_q), 164.92 (CO), 165.11 (CO), 171.94 (CO). MALDI-TOFMS (2,5-dihydroxybenzoic acid): 1799.0 $(M + H)^+$, 1820.9 $(M + Na)^+$.

***N,N′*-(4-Tritylphenyl)sebacinamide (free axle of 14).** Colorless solid. Yield: 63 mg (11%). Mp: 294 °C. R_f 0.55 (CH_2Cl_2/ethyl acetate 20:1). ^{1}H NMR (250 MHz, DMSO-d_6) δ 1.26 (8H, br), 1.55 (4H, br), 2.25 (4H, t, J = 7.3 Hz), 7.02 and 7.47 (8H, AA′BB′,), 7.12 (12H, d, ^3J = 7.4 Hz), 7.18 (6H, t, J = 7.0 Hz), 7.28 (12H, t), 9.86 (2H, s, NH). MALDI-TOFMS (2,5-dihydroxybenzoic acid): 837.7 $(M + H)^+$, 859.7 $(M + Na)^+$. Anal. Calcd for $C_{60}H_{56}N_2O_2 \cdot 0.5H_2O$: C, 85.17; H, 6.79; N, 3.31. Found: C, 85.00; H, 6.74; N, 3.26.

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