Self-Assembly and Dynamics of [2]- and [3]Rotaxanes with a Dinuclear Macrocycle Containing Reversible Os–N Coordinate Bonds

Sung-Youn Chang, Jeung Soon Choi, and Kyu-Sung Jeong*[a]

Abstract: With a dinuclear macrocycle **2** that contains weak reversible Os^{VI}–N coordinate bonds, self-assembly and equilibrium dynamics of [2]- and [3]rotaxanes have been investigated. When the macrocycle **2** was mixed together with threads **4a**–**e**, which all contain an adipamide station but different sizes of end groups, [2]pseudorotaxane- and rotaxane-like complexes were immediately formed with large association constants of $> 7 \times 10^3\,M^{-1}$ in $CDCl_3$ at 298 K. Exchange dynamics, explored by 2D-EXSY experiments, suggest that assembly and disassembly of complexes occur through two distinct pathways, slipping or clipping, and this depends on the size of the end groups. The slipping pathway is predominant with smaller end groups that give pseudorotaxane-like complexes, while the clipping pathway is observed with larger end groups that yield rotaxane-like complexes. Under the same conditions, exchange barriers ($\Delta G^{\neq}$) were 14.3 kcal mol^{-1} for **4a** and 16.7 kcal mol^{-1} for **4d**, and indicate that the slipping process is at least one order of magnitude faster than the clipping process. Using threads **13a** and **13b** that contain two adipamide groups, more complicated systems have been investigated in which [2]rotaxane, [3]rotaxane, and free components are in equilibrium. Concentration- and temperature-dependent ^1H NMR spectroscopic studies allowed the identification of all possible elements and the determination of their relative distributions in solution. For example, the relative distribution of the free components, [2]rotaxane, and [3]rotaxane are 30, 45, and 25%, respectively, in a mixture of **2** (2 mM) and **13a** (2 mM) in $CDCl_3$ at 10 °C. However, [3]rotaxane exists nearly quantitatively in a mixture of **2** (4 mM) and **13a** (2 mM) in $CDCl_3$ at a low temperature −10 °C.

Keywords: coordination modes · macrocycles · rotaxanes · self-assembly · supramolecular chemistry

Introduction

Rotaxanes and pseudorotaxanes are chemical entities comprising macrocycles (beads) and linear molecules (threads), they contain mutual recognition sites and consequently assemble in a threading mode.[1, 2] In rotaxanes, bulky stoppers at the ends of the thread prevent dissociation into the individual components. In contrast, pseudorotaxanes have small end groups, and can be reversibly converted into the free components. Both supermolecules have unique properties and are at the frontier in the construction of molecular-level machines.[3, 4] The intrinsic high kinetic stability of the rotaxanes makes it easy to control and define their motion and function. The synthesis of the pseudorotaxanes, on the other hand, is much simpler in that they self-assemble from a mixture of individual components. In addition, the pseudorotaxanes display more diverse motional modes associated with their reversible assembly and disassembly. Incorporation of these pseudorotaxane features into the rotaxanes may eventually yield more sophisticated and versatile, but readily accessible, supramolecular machines. One way to accomplish this goal would be to replace one or more of the covalent bonds in either the macrocycle or linear molecules with reversibly controllable, weak bonds.[5] Among possible weak bonds, the coordinate bond may be the most suitable because both the bond strength and geometry are tunable with the selection of the right combination of metal and ligands.

A number of coordinate-bond-based rotaxanes have been described thus far, but in all cases the bond between the transition metal and ligand was used for either attaching stoppers to the thread or connecting one thread with another.[6] Although a variety of macrocycles that possess reversible coordinate bonds have been prepared by self-assembly over the last decade,[7] none has been used for the construction of rotaxanes. We recently described the rotaxane complex **1**·**4d** derived from the macrocycle **1** which contains two reversible Os^{VI}–N coordination bonds at one corner.[8]

Herein we report our continued efforts to devise rotaxanes that reversibly assemble from and disassemble into their components under thermodynamic conditions. Instead of using the mononuclear macrocycle **1** as a bead component the

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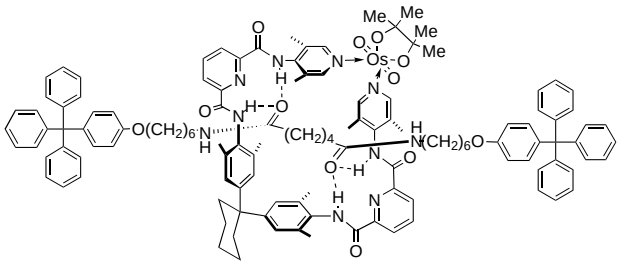

1·4d

dinuclear macrocycle **2** was used (Figure 1) because it was found to have several advantages for this study. First, the symmetrical nature of macrocycle **2** makes it much easier to synthesize than **1**. Second, **2** shows at least an order of magnitude higher affinity toward the threads than **1**, and consequently the relative population of the resulting rotaxane is dramatically increased in solution. This high affinity between thread and bead molecules is a critical factor required for the efficient construction of [*n*]rotaxanes with multiple beads.[9] The thread molecules studied here contain one or two adipamide station(s), as well as different sizes of end groups. The dynamics of the exchange processes, studied by ^{1}H NMR spectroscopy, suggest that pseudorotaxanes and rotaxanes are reversibly formed by two distinct pathways, slipping and clipping. Furthermore, with the two-station threads we also describe more intricate systems wherein [2]rotaxane, [3]rotaxane, and free components exist in equilibrium. The relative distribution of these components in solution can be tuned by simply adjusting the ratio of bead and thread components.

Abstract in Korean : 약하고 가역적인 Os^{VI}–N 배위결합을 포함한 이핵 거대고리 **2** 를 이용하여, [2]-, [3]로탁세인의 자기조립과 평형 동력학을 조사하였다. 거대고리 **2** 를 아디프아마이드 역을 포함하고 서로 다른 크기의 마개를 갖는 실분자 **4a–e** 와 섞으면, [2]유사로탁세인과 로탁세인 복합체가 즉시 형성되는데, 그 회합상수는 298 K, $CDCl_3$ 에서 > 7×10^3 M^{-1} 로 매우 크다. 교환 동력학은 2D-EXSY 실험으로 밝혔으며, 그 결과에 의하면 복합체의 조립과 분해는 실분자의 양끝에 있는 마개의 크기에 따라 두 가지 서로 다른 경로 -미끄러짐과 집게과정- 를 통하여 일어난다. 마개가 작아서 유사로탁세인 복합체를 형성하는 경우 미끄러짐 과정이 우세하고, 마개가 커서 로탁세인 복합체를 형성할 때는 집게 과정이 우세하다. 같은 조건에서 교환 에너지 벽($\Delta G^{\ddagger}$)은 **4a** 에 대해서 14.3 kcal M^{-1}, **4d** 에 대해서는 16.7 kcal M^{-1} 이다. 이는 미끄러짐 과정이 집게 과정보다 최소 10 배 이상 빠르다는 것을 나타낸다.

두 개의 아디프아마이드 기를 포함한 실분자 **13a**, **13b** 를 사용해서 [2]로탁세인, [3]로탁세인, 자유 구성분자가 평형을 이루고 있는 좀 더 복잡한 시스템에 대해 연구했다. 농도 및 온도 의존 ^{1}H NMR 분광 연구를 통하여, 용액에 존재하는 모든 성분을 확인하였으며 그 상대 분포를 결정하였다. 예를 들어, 10 °C, $CDCl_3$ 용액에서 **2**(2 mM) 와 **13a**(2 mM)가 섞여 있을 때, 구성분자, [2]로탁세인, [3]로탁세인의 상대분포는 각각 30%, 45%, 25% 였다. 그러나 **2**(4 mM)와 **13a**(2 mM)을 섞어 온도를 - 10 °C 로 낮추면, [3]로탁세인이 정량적으로 형성된다.

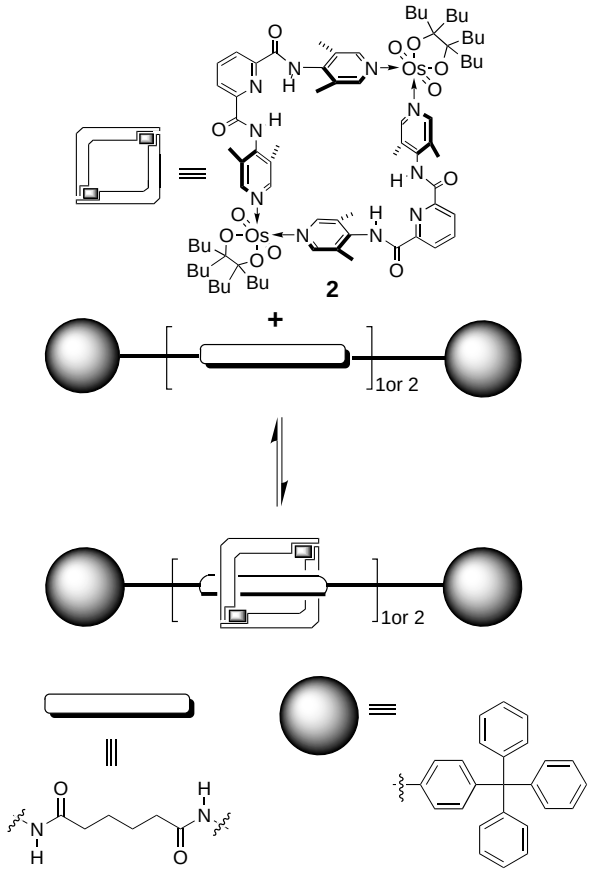

Figure 1. Schematic representation for the reversible formation of rotaxanes studied here.

Results and Discussion

Design and synthesis: The macrocycle **2** was spontaneously assembled from a mixture of osmium tetraoxide, 5,6-dibutyl-5-decene, and bispyridyl ligand as described previously.[10] Here, a symmetrical tetra-substituted olefin, 5,6-dibutyl-5-decene,[11] was chosen in order to 1) increase the solubility of **2** in organic solvents, 2) increase the stability of **2** upon contact with air and protic solvents, and 3) avoid the production of a diastereomeric mixture of **2**. The macrocycle **2** contains a well-defined square cavity in which four hydrogen donors (NHs) are inwardly directed by virtue of internal N (central pyridine)···H–N (amide) hydrogen bonds.[12] During the course of extensive binding studies, adipamide derivatives were found to bind strongly and selectively to the cavity of **2**.[10] This functionality was therefore employed in all threads as the station for **2**. To minimize possible steric repulsion and thus maximize the association between **2** and threads, the adipamide station was separated from the bulky stoppers by inserting either a hexyl or a tri(ethylene glycol) chain between them. The threads thus prepared could be categorized into three different types on the basis of the number of stations inside and the similarity of the end groups.

Symmetrical one-station threads 4a–e: Syntheses of threads **4b–e** were straightforward and are outlined in Scheme 1.

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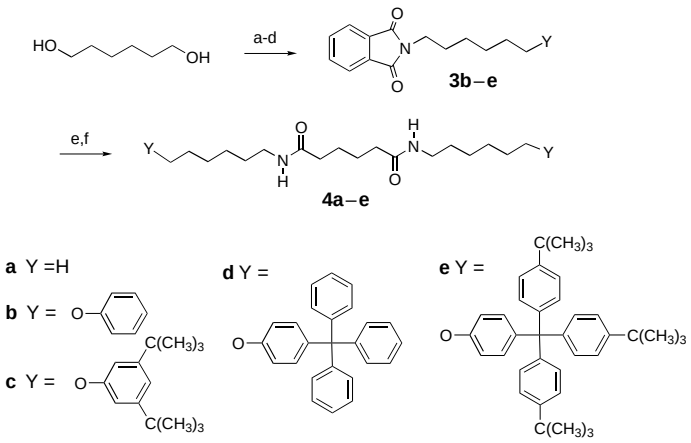
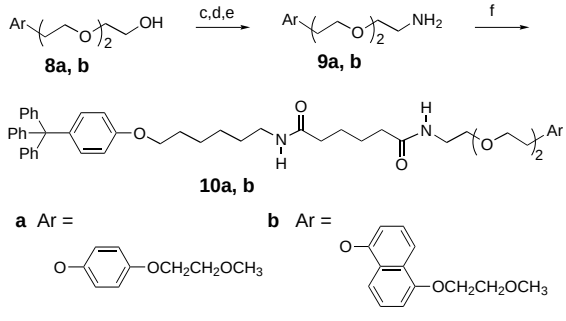


Scheme 1. Synthesis of threads **4b–e**. Reagents and conditions: a) toluene-*p*-sulfonyl chloride, Et_3N, THF, 0 °C 1 h, 37%; b) phenols (H·**b–e**), K_2CO_3, DMF or acetonitrile, 60–70 °C, 5–16 h, 76–82%; c) toluene-*p*-sulfonyl chloride, Et_3N, CH_2Cl_2, 0 °C to RT, 5–19 h, 77–84%; d) phthalimide, K_2CO_3, DMF, 60–70 °C; 9–17 h, 72–94%; e) $H_2NNH_2 \cdot H_2O$, EtOH, reflux, 4 h; f) adipoyl chloride or bis(pentafluorophenyl) adipate, Et_3N, CH_2Cl_2, 0 °C to RT, 2–4 h, 40–76%.

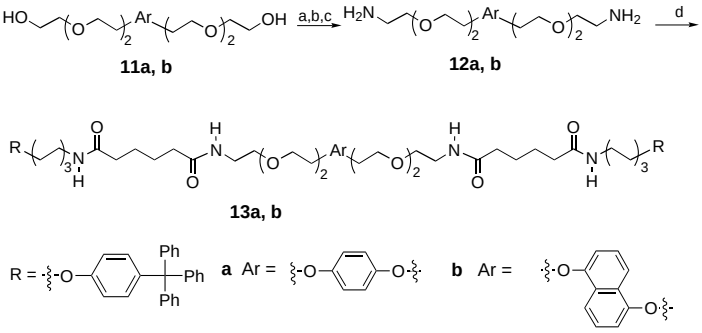
Stepwise tosylations followed by sequential displacements of hexane-1,6-diol with phenols and phthalimide under basic conditions gave the amine precursors **3b–e**. After treatment with hydrazine, the resulting amines were coupled with adipoyl chloride or pentafluorophenyl diester to give the threads **4b–e**. In addition, the thread of hexanedioic acid bishexylamide (**4a**) was prepared in 67% yield by coupling adipic acid with 1-aminohexane.

Unsymmetrical one-station threads 10a and 10b: Adipamide monoacid **7** was obtained by the coupling of amine **5** with acid **6** in the presence of 2,2-dimethylpropionyl chloride (Scheme 2), followed by catalytic debenzylation (H_2, 5% Pd/C). The compounds **8a** and **8b**, obtained from 1,4-dihydroxybenzene and 1,5-dihydroxynaphthalene, were converted into the corresponding amines **9a** and **9b**. Finally, coupling reactions of **7** with **9a** or **9b** in the presence of 2,2-dimethylpropionyl chloride gave the threads **10a** and **10b**, respectively.



Scheme 2. Synthesis of threads **10a** and **10b**. Reagents and conditions: a) 2,2-dimethylpropionyl chloride, Et_3N, CH_2Cl_2, 73%; b) 5% H_2/Pd-C, MeOH/EtOAc, 88%; c) toluene-*p*-sulfonyl chloride, Et_3N, CH_2Cl_2, RT, ca. 20 h, 69–79%; d) phthalimide, K_2CO_3, DMF, 60–70 °C; 6 h, 70–76%; e) $H_2NNH_2 \cdot H_2O$, EtOH, reflux, 4 h; f) 2,2-dimethylpropionyl chloride, Et_3N, CH_2Cl_2, 0 °C to RT, 1 h, then **7**, RT, 1 h, 51–54%.

Two-station threads 13a and 13b: As outlined in Scheme 3, threads **13a** and **13b** were prepared by similar reaction sequences used for **10a** and **10b**.



Scheme 3. Synthesis of threads **13a** and **13b**. Reagents and conditions: a) toluene-*p*-sulfonyl chloride, Et_3N, CH_2Cl_2, RT, ca. 24 h, 82–94%; b) phthalimide, K_2CO_3, DMF, 60–70 °C; ~30 h, 73%; c) $H_2NNH_2 \cdot H_2O$, EtOH/CH_2Cl_2, reflux, 8 h; d) **7**, 2,2-dimethylpropionyl chloride, Et_3N, CH_2Cl_2, 0 °C to RT, 1 h, then **12a–b**, RT, 1 h, 38%–63%.

Association constants between macrocycle 2 and threads 4a–e: When macrocycle **2** and each of threads **4c**, **4d**, and **4e** were mixed together in $CDCl_3$, a new set of ^1H NMR signals corresponding to the complexes could immediately be seen at room temperature (Figure 2d). On the basis of ^1H NMR integration of five different stock solutions ranging in the concentration from 5.0 to 0.2 mM in $CDCl_3$, the average association constants ($K_a \pm 20\%$) of **2** with **4c**, **4d**, and **4e** were calculated to be 8900, 8400, and 7200 M^{-1}, respectively (Table 1). With threads **4a** and **4b**, in which there are small end groups, association constants could not be accurately determined because the free and complex components gave considerably broadened and weight-averaged ^1H NMR spectra at room temperature (Figure 2b). Therefore, the association constants for **4a** and **4b** were estimated by dilution experiments. When a 5 mM $CDCl_3$ solution of each component was diluted to 0.5 mM, changes in the chemical shifts were negligible (that is, the NH proton of **2**, $\Delta\delta < 0.1$ ppm relative to $\Delta\delta_{max} = 1.5$ ppm), and this suggests $K_a > 1 \times 10^4\ M^{-1}$ for threads **4a** and **4b**.

Two trends observed in the binding affinities are worthy of note. First, the magnitudes of the association constants depend slightly on the size of the end groups on the threads. As the stopper size increases the association constant decreases, possibly owing to a weak steric repulsion between the macrocycle and end groups. Second, the association constants for **2** and the threads are much higher than the constants obtained with mononuclear macrocycle **1** under the same conditions, as seen in the Table 1. The enhanced affinity of the dinuclear macrocycle **2** is probably a result of the

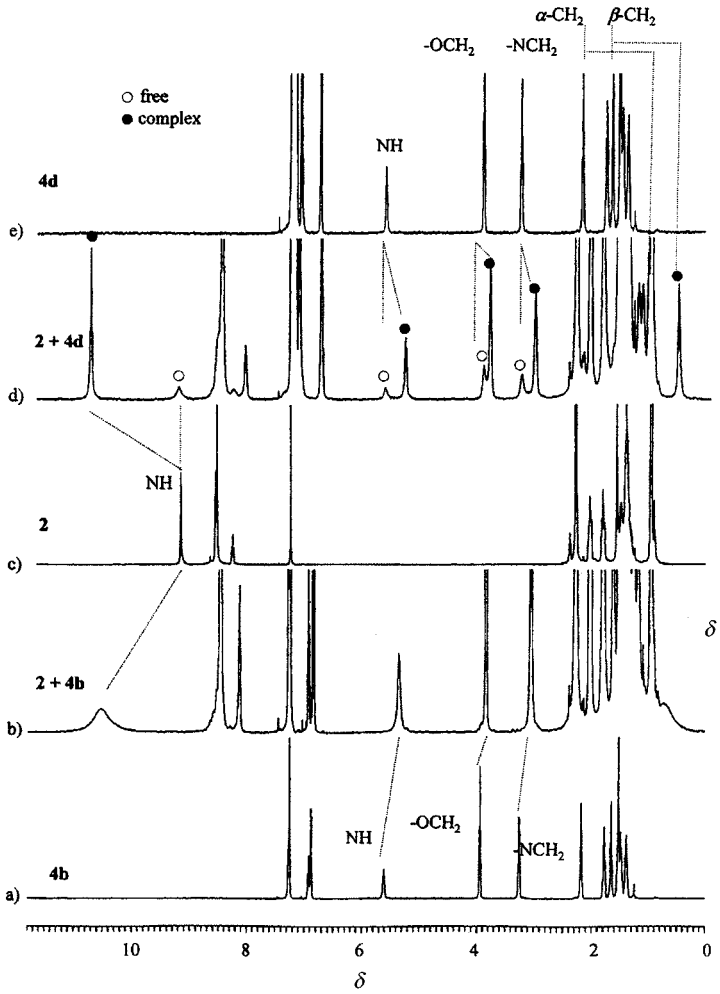


Figure 2. ^{1}H NMR (500 MHz) spectra in $CDCl_3$ at 25 °C of a) **4b**, b) **4b** (2 mM) + **2** (2 mM), c) **2**, d) **4d** (2 mM) + **2** (2 mM), and e) **4d**.

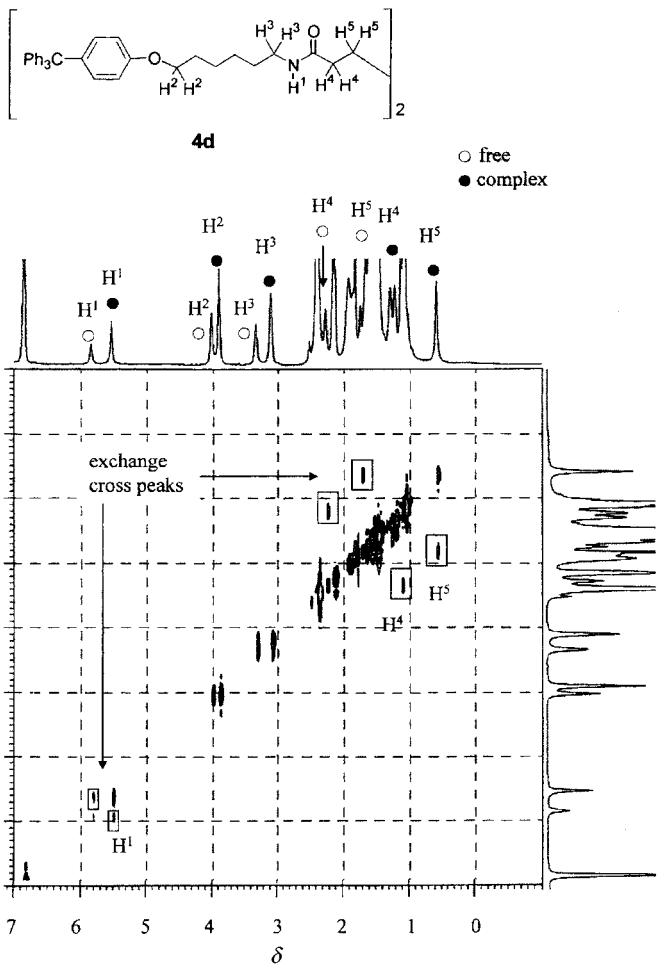


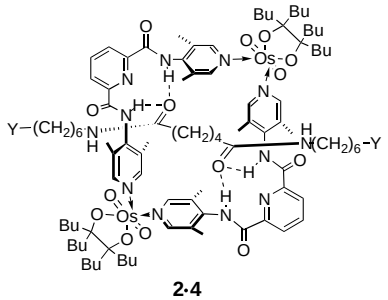
Figure 3. 2D-EXSY spectrum obtained with **2** (10 mM) and **4d** (15 mM) at 25 °C in $CDCl_3$ using mixing time (τ_m) of 50 ms, indicating that the exchange occurs between complex **2·4d** and its free components.

Table 1. Association constants ($K_a \pm 20\%$, M^{-1}) of macrocycles **1** and **2** with one-station threads **4a–e** in $CDCl_3$ at 25 °C.

Thread	K_a (M^{-1})	
	Macrocycle **1**	Macrocycle **2**
4a	1300	$>1\times10^4$
4b	900	$>1\times10^4$
4c	520	8900
4d	520	8400
4e	not determined	7200

coordination of all four lutidines to the osmium centers, which in turn leads to an increased hydrogen bonding donor ability of the amide NHs inside the cavity of **2**.

Spectroscopic evidence for formation of pseudorotaxanes and rotaxanes 2·4: As shown in Figure 2, the ^{1}H NMR spectra of complexes **2·4** are clearly different from their free components. The NH signal of **2** was significantly shifted downfield ($\Delta\delta = \approx 1.5$ ppm) as a result of strong hydrogen bond formation. In addition, the signal for CH hydrogens (see H^4 and H^5 in Figure 3) α and β to the carbonyls in the adipamide station of **4** appeared at the far-upfield region of $\delta = 1.1$ and 0.5, respectively, compared with $\delta = 2.2$ and 1.7 for the free **4**. These spectroscopic changes are nearly identical to those observed on the formation of a pseudorotaxane complex between mononuclear macrocycle **1** and thread **4a**, the structure of the complex **1·4** was previously confirmed by X-ray crystal analysis.[8] Further information on the structure of complexes **2·4** was obtained from kinetic exchange studies



2·4

between complexes **2·4** and their free components (discussed later). The 2D-EXSY experiments[13] suggest that the exchange rates are faster in the cases of pseudorotaxane-like complexes, but are slower for rotaxane-like complexes. In

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other words, the kinetic stability of the complex increases as the size of the end group increases, as expected for pseudorotaxane or rotaxane formation.[14, 15] As mentioned in the binding studies, the opposite is true in the thermodynamic stability of the complexes. All of the observations described thus far are consistent with a proposed structure of complexes **2·4** in which the macrocycle **2** encircles the adipamide station of the threads, and consequently forms pseudorotaxanes or rotaxanes.[16]

Dynamics of exchange between complexes 2·4 and their components: Two possible pathways may be considered for the reversible formation of pseudorotaxane or rotaxane complexes (Figure 4). One is a slipping process where threads

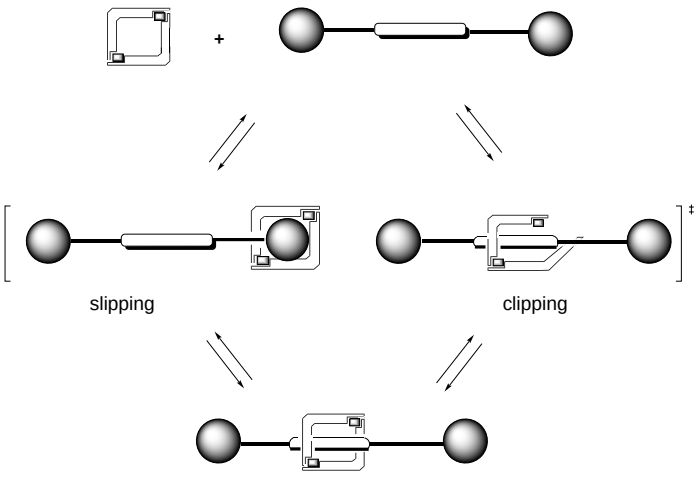

Figure 4. Schematic representation of two possible pathways, slipping and clipping, for assembly and disassembly of pseudorotaxane or rotaxane complexes.

4 slide in and out though the cavity of macrocycle **2**. This pathway is only possible when the size of the end group is smaller than the size of the cavity. Another is a clipping process that requires the dissociation of the Os^{VI}–N coordinate bond in **2**, followed by the formation of intermediate complexes, and finally the reconstruction of the coordinate bond. The two pathways, slipping and clipping, are expected to have different activation barriers, the latter process depends more on the strength of the coordinate bond in the macrocycle, rather than on the size of the end groups in the thread.

As mentioned earlier, broad and weight-averaged ^{1}H NMR signals were observed at room temperature when the macrocycle **2** was mixed with threads **4a** and **4b**, while sharp and separated signals were seen with threads **4c**, **4d**, and **4e**. This spectral difference must be closely related to the exchange rate between complexes and their free components. Qualitatively, the exchange rates are relatively fast on the NMR time scale in threads **4a** and **4b** with smaller end groups, but slow in threads **4c**, **4d**, and **4e** with bulkier end groups. Corey–Pauling–Koltun (CPK) models show that the threads **4a** and **4b** can penetrate into the cavity of **2**, but the end groups in the threads **4c**, **4d**, and **4e** are too bulky to pass through the cavity without breaking at least one of the coordinate bonds in **2**. To obtain quantitative data on the dynamics of the exchange between the complexes and their components, we performed coalescence temperature[17] and 2D-EXSY experiments (Table 2).[13] With threads **4a** and **4b**, the values are in the range of 13.1–13.6 kcal mol^{-1} at 286–302 K based on the coalescence temperature method. However, based on the EXSY experiments, the values with threads **4c**, **4d**, and **4e** suddenly increase to ≈15.5 kcal mol^{-1} at 298 K. This value remains constant despite an increase in the steric bulkiness of the end groups from **4d** to **4e**. The activation energy ($\Delta G^{\neq}$) for the exchange depends on the temperature. Therefore, we determined and compared the activation barriers at the same temperature 283 K, at which the free components and complex gave well-resolved separate ^{1}H NMR signals regardless of the end group size on the threads **4**. The threads **4a** and **4d** were chosen as representative examples of small and large end groups, respectively. The exchange energies ($\Delta G^{\neq}$) at 283 K, determined by EXSY experiments, were 14.3 kcal mol^{-1} for **4a** and 16.7 kcal mol^{-1} for **4d**, and these values correspond to exchange rates (k) of ≈50 and 0.8 s^{-1}, respectively. Both slipping and clipping pathways are possible with **4a**, but only a clipping pathway is possible with **4d**, therefore, it is clear that the slipping process is at least an order of magnitude faster than the clipping process under the same conditions.

Table 2. Activation barriers [$\Delta G^{\neq}$] of exchange between complexes and their free components **2** and one-station threads **4a–e**, **10a**, and **10b**.

Entry	Thread	Method[a]	Temp. [°C]	$\Delta G^{\neq}$[kcal mol^{-1}][b]
1	**4a**	coalescence	13–27	13.1–13.5
2		EXSY	10	14.3
3	**4b**	coalescence	16–29	13.2–13.6
4	**4c**	EXSY	25	15.3
5	**4d**	EXSY	25	15.5
6		EXSY	10	16.7
7	**4e**	EXSY	25	15.5
8	**10a**	EXSY	10	14.9
9	**10b**	EXSY	25	15.2

[a] For 2D-EXSY experiments, the concentration of each macrocycle and thread is 10–20 mM in $CDCl_3$ with the molar ratio of 0.7 or 1.5, and the mixing time (τ_m) is 50 ms except entry 6 (300 ms) and entry 9 (80 ms). [b] Errors are within ±0.2 kcal mol^{-1}.

Complex formation between macrocycle 2 and unsymmetrical threads 10a and 10b: The unsymmetrical one-station threads **10a** and **10b** were prepared as a reference for two-station threads **13a** and **13b**. When **10a** and **10b** were added to a $CDCl_3$ solution of the macrocycle **2**, the observed ^{1}H NMR spectral changes were consistent with the formation of complexes by hydrogen bonding as described earlier with the symmetrical threads **4a–e**. However, owing to the unsymmetrical nature of threads **10a** and **10b**, some ^{1}H NMR signals of the macrocycle **2** become further split at lower temperatures when complexed. For example, the four amide NH protons of **2** split into two singlets at 0 °C, otherwise all protons appear at the same resonance (Figure 5).

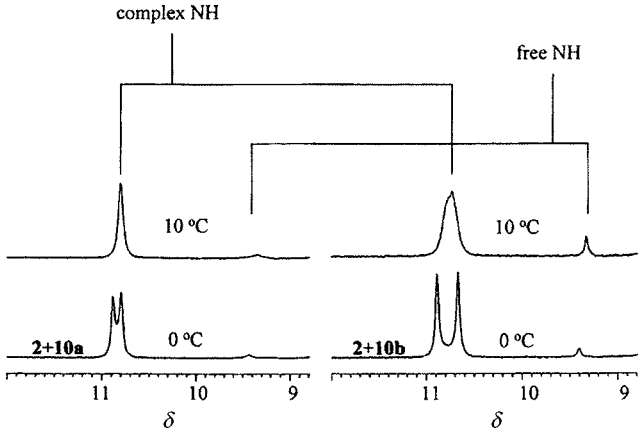

Figure 5. Partial ^{1}H NMR (500 MHz) spectra of the amide NH signals of macrocycle **2**, which split into two singlets when complexed with unsymmetrical threads **10a** (left) and **10b** (right) in $CDCl_3$ at a low temperature (0 °C).

The ^{1}H NMR spectra also depend on the size of the aryl groups at one end, phenyl versus naphthyl, as seen in Figure 6. With the thread **10a** (2 mM in $CDCl_3$) with the smaller phenyl group, a broad and poorly resolved ^{1}H NMR spectrum was

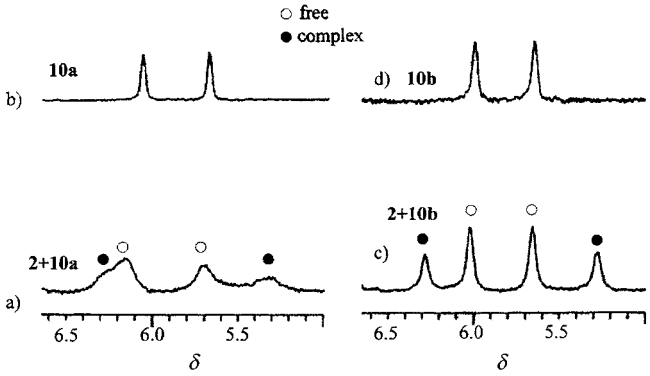

Figure 6. Partial ^{1}H NMR (500 MHz) spectra in the region of the thread NH signals; a) **10a** (2 mM) + **2** (1 mM), b) **10a** (2 mM), c) **10b** (2 mM) + **2** (1 mM), and d) **10b** (2 mM) in $CDCl_3$ at 25 °C.

obtained at room temperature when approximately 0.5 equivalents of the macrocycle **2** were added. On the other hand, sharp and well-resolved signals of both complex and the free components were observed in the case of the naphthyl-ended thread **10b**. The activation energies ($\Delta G^{\ddagger}$) for assembly and disassembly were determined by 2D-EXSY experiments and found to be 14.9 kcal mol^{-1} at 283 K for **2** and **10a**, and 15.2 kcal mol^{-1} at 298 K for **2** and **10b**. These values suggest that the slipping process dominates in the small phenyl-ended thread **10a**, while the clipping process is preferred in the large naphthyl-ended thread **10b**.

Equilibrium between [2]rotaxane and [3]rotaxane derived from two-station threads 13a and 13b: Possible equilibria and processes between macrocycle **2** and two station threads **13a** and **13b** are schematically summarized in Figure 7. As discussed earlier, bulky tritylphenyl groups at both termini

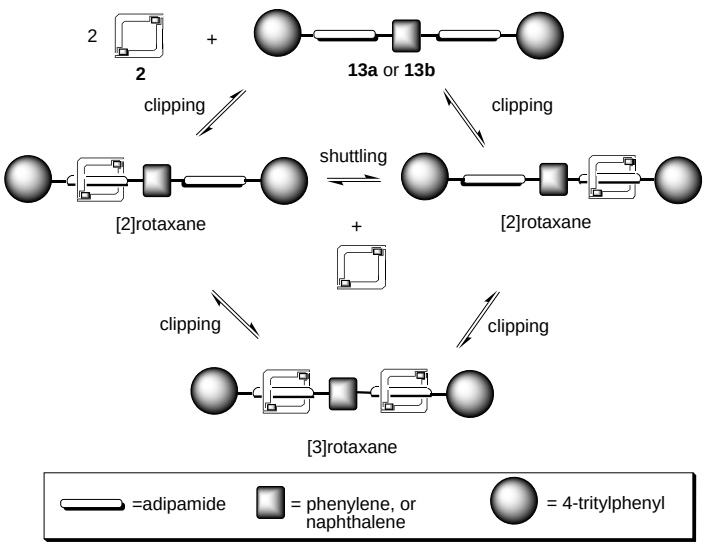

Figure 7. Possible equilibria and processes between [2]rotaxane, [3]rotaxane, and their free components, macrocycle **2** and two-station threads **13a** and **13b**.

of threads **13a** and **13b** prevent the slipping in and out, but allow the clipping on and off of the macrocycle **2**.

When two-station threads **13a** and **13b** and the macrocycle **2** were mixed together in $CDCl_3$, the ^{1}H NMR spectral behavior was similar to that observed for the one-station threads and the reference threads described above. Therefore, [2]rotaxane, [3]rotaxane, and their free components could be clearly identified by ^{1}H NMR spectroscopy. The two most diagnostic signals are the amide NH protons of both macrocycle **2** and thread **13a** or **13b**. The NH signal of the complexed **2** was split into four singlets at −10 °C; two singlets each for the [2]- and [3]rotaxane (Figure 8). As the concen-

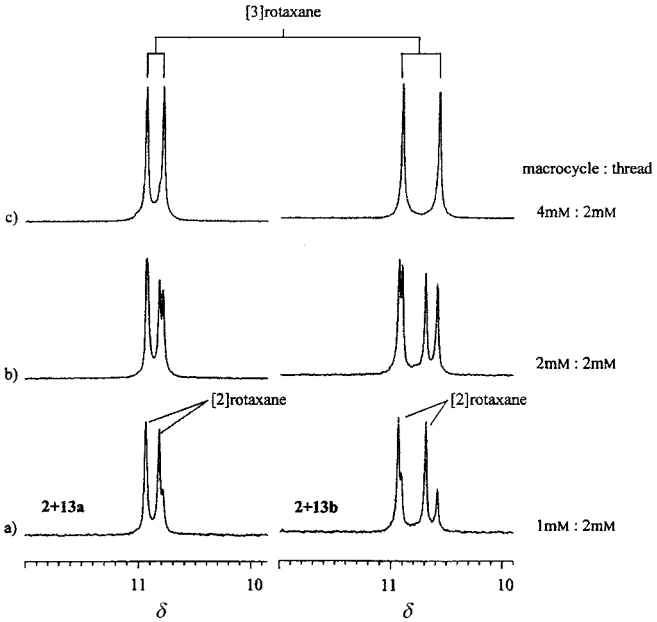

Figure 8. Partial ^{1}H NMR (500 MHz) spectra of the amide NH signals of macrocycle **2** when complexed with two-station threads **13a** (left) and **13b** (right) in $CDCl_3$ at −10 °C; a) macrocycle (1 mM) and thread (2 mM), b) macrocycle (2 mM) and thread (2 mM), and c) macrocycle (4 mM) and thread (2 mM).

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tration of **2** increased from 1 to 4 mM, a set of two singlets was initially dominant, then nearly equal to, and eventually replaced by another set of singlets. It is therefore clear that [2]rotaxane corresponds to the initial set, and [3]rotaxane to the later set of signals. Additional information for each component in solution can be obtained from the thread NH signals in the region between $\delta = 5$ and 7 in the ^{1}H NMR spectra (Figure 9). In the [2]rotaxane, one station of the thread

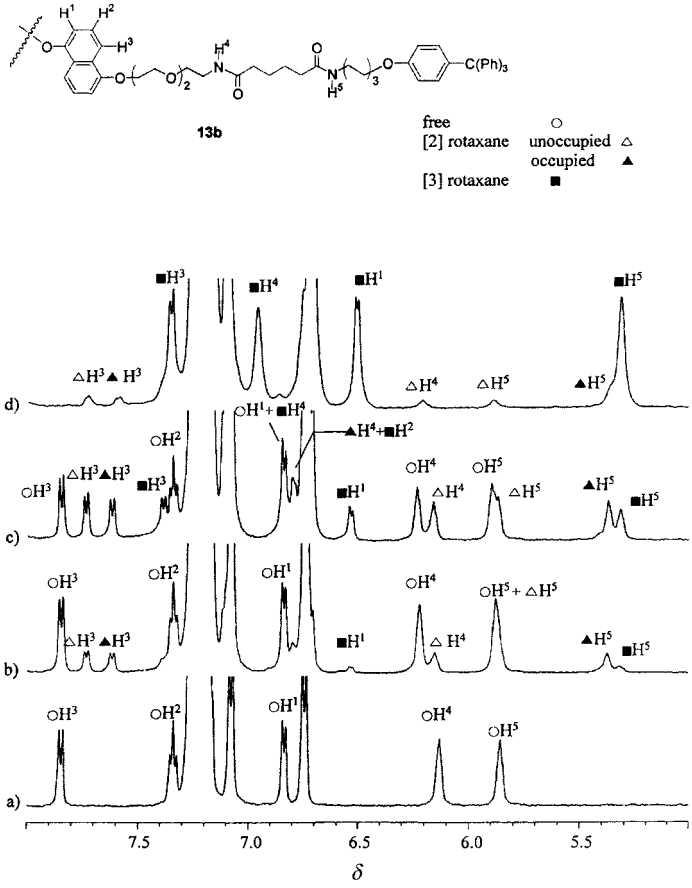

Figure 9. Partial ^{1}H NMR (500 MHz) spectra of a mixture of **2** + **13b** in $CDCl_3$ at 10 °C; a) **13b** (2 mM), b) **13b** (2 mM) and **2** (1 mM), c) **13b** (2 mM) and **2** (2 mM), and d) **13b** (2 mM) and **2** (4 mM).

is occupied by the macrocycle **2**, but the other is unoccupied. Fortunately, the NH signals for the occupied station of [2]rotaxane appear at the different position from those of [3]rotaxane. Likewise, the unoccupied station of [2]rotaxane and the free thread **13a** or **13b** give separate signals for the amide NH protons in ^{1}H NMR spectroscopy. For the example of **2** and **13b** (2 mM of each in $CDCl_3$) at 10 °C, two NH signals for the occupied station of [2]rotaxane appear at $\delta = 6.80$ and 5.37, and signals for the unoccupied one appear $\delta = 6.16$ and 5.87. On the other hand, two NH signals of [3]rotaxane appear at $\delta = 6.85$ and 5.31, and the signals of free thread **13b** appear at $\delta = 6.23$ and 5.90 under the same conditions. This spectral behavior makes it possible to analyze the relative distribution of [2]rotaxane, [3]rotaxane, and the free component (Table 3). For example, distributions of the free, [2]rotaxane, and [3]rotaxane are 32, 49, and 19%, respectively, in a mixture of **2** (2 mM) and **13b** (2 mM) in $CDCl_3$ at 10 °C. In addition, the

Table 3. Relative distributions [%][a] of the free, [2]rotaxane and [3]rotaxane in a mixture of macrocycle **2** and two-station threads **13a** and **13b** in $CDCl_3$ at 10 °C.

Entry	Thread (2 mM)	Concentration of **2**	Free	[2]Rotaxane	[3]Rotaxne
1	**13a**	1 mM	58	34	8
2	**13a**	2 mM	30	45	25
3[b]	**13a**	4 mM	≈0	16	84
4	**13b**	1 mM	58	37	5
5	**13b**	2 mM	32	49	19
6[b]	**13b**	4 mM	≈0	16	84

[a] Relative distributions were estimated by the ^{1}H NMR integration of the thread NH signals, and errors in the integration are within 15%. [b] Upon cooling the solution down to −10 °C, [3]rotaxane could only be seen and other components are negligible in the ^{1}H NMR spectrum.

relative populations of [2]- and [3]rotaxane become 16 and 84%, respectively, by increasing the concentration of **2** to 4 mM (1 equivalent based on the number of adipamide stations) under the same conditions, and eventually [3]rotaxane exists nearly quantitatively upon cooling the solution down −10 °C. This clearly shows that the relative population of the components in solution could be varied by adjusting molar ratios, concentrations, and/or temperature.

The phenylene and naphthalene groups in the middle of **13a** and **13b** are inserted in order to control a possible shuttling process of [2]rotaxane,[18] an assembly of **13a** (or **13b**) with one macrocycle **2**. It was difficult, however, to notice the difference in ^{1}H NMR spectra between threads **13a** and **13b** at various conditions when mixed together with **2**, except the thread **13b** gives better-resolved signals under the same conditions. Attempts to sort out exchange dynamics between [2]rotaxane, [3]rotaxane, and the free components were not successful because the peak separation between components was too small to give satisfactory 2D-EXSY results. The studies with the reference threads **10a** and **10b** provide, at this moment, indirect evidence for the possibility of the shuttling process of the [2]rotaxane; the macrocycle **2** may shuttle back and forth across the smaller phenylene, but not the larger naphthalene group.

Conclusion

Reversibility and self-assembly are two main features in natural systems. Recently, much effort has been carried out in the area of supramolecular chemistry to incorporate these important characteristics into artificial counterparts. In this context, we herein describe the self-assembly of rotaxane complexes in solution at ambient conditions. The reversibility stems from the weak Os^{VI}–N coordinate bonds of macrocycle **2**, a bead molecule that was also spontaneously assembled from its constituents. The macrocycle **2** strongly binds ($K_a > 7 \times 10^3$ M^{-1} in $CDCl_3$ at 298 K) in a threading mode to threads **4a**–**e** that all contain an adipamide station but different sizes of end groups. Exchange dynamics, studied by 2D-EXSY experiments, clearly show that the processes of complexation and decomplexation switch from slipping to clipping when the end groups of **4a**–**e** are bulkier than the cavity size of the

macrocycle **2**. Finally, two-station threads **13a** and **13b** give us an opportunity to study a more complicated equilibrium system of [2]rotaxane, [3]rotaxane, and free components. All of these possible components could be clearly identified in $CDCl_3$, and their distributions were therefore estimated by ^{1}H NMR spectroscopy. At a low ratio of **2** to **13a** (or **13b**), [2]rotaxane was a major component, while [3]rotaxane was predominant at a higher ratio, as expected. The reversibility in our system inevitably results in a decrease in the kinetic stability of individual components. We are currently pursuing systems that balance these contradictory properties for the self-assembly of molecular machines, for example, shuttles that respond to outside stimuli.

Experimental Section

General methods: All reagents were, unless otherwise noted, used as received. Chloroform, dichloromethane, and acetonitrile were distilled under nitrogen from calcium hydride (CaH_2), diethyl ether, and tetrahydrofuran from Na/benzophenone, and triethylamine from KOH. Dimethylformamide (DMF) was distilled under reduced pressure after drying with anhydrous magnesium sulfate ($MgSO_4$). Melting points were determined by using a Mel-Temp II capillary melting point apparatus and were uncorrected. Infrared spectra were obtained on a Nicolet impact 410 FT-IR spectrometer. All NMR spectra were recorded on a Bruker DPX-250 or DRX-500 spectrometer and chemical shifts were reported in ppm downfield relative to the residual protonated solvent peaks ($CHCl_3$: 7.26 ppm for ^{1}H NMR spectra, 77 ppm for ^{13}C NMR spectra). Mass spectra were obtained with a JMS-HS 110/110A mass spectrometer (JEOL inc., Japan) and nitrobenzyl alcohol was used as a matrix in $CHCl_3$ as solvent.

Macrocycle 2: The macrocycle was prepared by following the procedure described previously.[10b] M.p. > 200 °C (decomp); ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 9.19$ (s, 4H; NH), 8.59 (d, $^3J(H,H) = 7.8$ Hz, 4H; Ar-H), 8.55 (s, 8H; Ar-H), 8.28 (t, $^3J(H,H) = 7.8$ Hz, 2H; Ar-H), 2.28 (s, 24H; CH_3), 2.08–1.98 (m, 8H; CH_2), 1.87–1.75 (m, 8H; CH_2), 1.52–1.29 (m, 32H; CH_2), 0.96 (t, $^3J(H,H) = 6.6$ Hz, 24H; CH_3); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 160.8$, 149.5, 148.6, 145.7, 131.5, 127.3, 94.4, 34.7, 27.5, 24.6, 16.9, 15.1; IR (KBr): $\tilde{\nu} = 3307$ (NH), 1691 (C=O), 829 (Os=O) cm^{-1}; FAB-MS: *m/z* (%): 1480 (0.017) $[M - (OC(C_4H_9)_2)_2]^+$, 1194 (0.034) $[M - 2(OC(C_4H_9)_2)_2]^+$; elemental analysis calcd(%) for $C_{78}H_{114}N_{10}O_{12}Os_2$(1764.3): C 53.10, H 6.51, N 7.94; found: C 53.15, H 6.57, N 7.98.

Hexane-1,6-dioic acid bis(hexylamide) 4a: A suspension of adipic acid (0.50 g, 3.42 mmol) in thionyl chloride (2.0 mL) containing a catalytic amount of DMF was heated at reflux for 2 h, and excess thionyl chloride was removed. The residue was dissolved in $CHCl_3$ (15 mL) and to this solution, 1-aminohexane (0.95 mL, 7.3 mmol, 2.1 equiv) and Et_3N (1.0 mL, 7.2 mmol, 2.1 equiv) were added at 0 °C (ice-water bath) under argon. The solution was stirred for 1 h at room temperature, then washed with saturated $NaHCO_3$ solution, brine, dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by column chromatography (MeOH/CH_2Cl_2 1:10) to give **4a** (0.72 g, 67%) as a white solid. M.p. 160 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 5.66$ (s, 2H; NH), 3.23 (m, 4H; NCH_2), 2.19 (t, $^3J(H,H) = 5.8$ Hz, 4H; $C(=O)CH_2$), 1.65 (m, 4H; CH_2), 1.49 (m, 4H; CH_2), 1.33–1.29 (m, 12H; CH_2), 0.88 (m, 6H; CH_3); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 172.8$, 39.7, 36.4, 31.6, 29.7, 26.7, 25.2, 22.7, 14.1; IR (KBr): $\tilde{\nu} = 3313$ (NH), 1632 (C=O) cm^{-1}; elemental analysis calcd(%) for $C_{18}H_{36}N_2O_2$ (312.49): C 69.18, H 11.61, N 8.96; found: C 69.21, H 11.60, N 8.96.

General procedure of 4b–e: Compounds **4b**, **4c**, **4d**, and **4e** were prepared in similar yields from hexane-1,6-diol in six steps. As a representative example the synthesis of **4b** is described below. To a solution of hexane-1,6-diol (30 g, 0.25 mol) in dry THF (70 mL) were added Et_3N (70 mL, 0.5 mol, 2 equiv) and toluene-*p*-sulfonyl chloride (48 g, 0.25 mol, 1 equiv) at 0 °C (ice-water bath) under argon. After stirring for 1 h at 0 °C, the solution was concentrated, the residue was taken up in CH_2Cl_2, washed with 1N HCl solution, saturated $NaHCO_3$ solution, and brine, and dried over anhydrous $MgSO_4$. The product was purified by column chromatography (EtOAc/*n*-hexane 1:1) to give toluene-4-sulfonic acid 6-hydroxyhexyl ester (26 g, 37% yield) as a colorless liquid. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.80$ (d, $^3J(H,H) = 8.2$ Hz, 2H; Ar-H), 7.35 (d, $^3J(H,H) = 8.0$ Hz, 2H; Ar-H), 4.02 (t, $^3J(H,H) = 6.4$ Hz, 2H; $ArOCH_2$), 3.60 (t, $^3J(H,H) = 6.4$ Hz, 2H; CH_2O), 2.45 (s, 3H; Ar-CH_3), 1.66 (m, 2H), 1.52 (m, 2H), 1.35–1.31 (m, 4H); elemental analysis calcd (%) for $C_{13}H_{20}O_4S$ (272.36): C 57.33, H 7.40; found: C 57.35, H 7.42.

A solution of toluene-4-sulfonic acid 6-hydroxyhexyl ester (5.0 g, 18.4 mmol), phenol (3.2 mL, 36.8 mmol, 2 equiv), and K_2CO_3 (7.6 g, 55 mmol, 3 equiv) in dry DMF (50 mL) was heated at 60–70 °C for 5 h under argon, and then the solution was filtered. The filtrate was concentrated, then taken up in ethyl acetate, and washed with H_2O, and brine and the residue was dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by column chromatography (EtOAc/*n*-hexane 1:1) to give 6-phenoxyhexane-1-ol (2.7 g, 76% yield) as a colorless liquid. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.30–7.24$ (m, 2H; Ar-H), 6.95–6.87 (m, 3H; Ar-H), 3.96 (t, $J = 6.4$ Hz, 2H; $ArOCH_2$), 3.67 (m, 2H; CH_2O), 1.80 (m, 2H), 1.61–1.53 (m, 2H), 1.48–1.41 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 159.2$, 129.5, 120.6, 114.6, 67.8, 63.0, 32.8, 29.4, 26.0, 25.7; elemental analysis calcd (%) for $C_{12}H_{18}O_2$ (194.27): C 74.19, H 9.34; found: C 74.17, H 9.34.

To a solution of 6-phenoxyhexan-1-ol (2.3 g, 11.8 mmol) in CH_2Cl_2 (40 mL) was added toluene-*p*-sulfonyl chloride (4.5 g, 23.6 mmol, 2 equiv) and Et_3N (4.9 mL, 2 equiv) at 0 °C under nitrogen. The mixture was stirred at room temperature under nitrogen for 6 h, then washed with HCl (1N) solution, saturated $NaHCO_3$, and brine then dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by column chromatography (EtOAc/*n*-hexane 1:4) to give toluene-4-sulfonic acid 6-phenoxyhexyl ester (3.3 g, 80%) as a colorless oil: ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta =$ 7.80 (d, $^3J(H,H) = 8.3$ Hz, 2H; Ar-H), 7.35 (d, $^3J(H,H) = 8.3$ Hz, 2H; Ar-H), 7.27–7.24 (m, 2H; Ar-H), 6.95–6.85 (m, 3H; Ar-H), 4.04 (t, $^3J(H,H) =$ 6.5 Hz, 2H; $ArOCH_2$), 3.91 (t, $^3J(H,H) = 6.4$ Hz, 2H; $ArOCH_2$), 2.44 (s, 3H; Ar-CH_3), 1.76–1.62 (m, 4H), 1.41–1.38 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 159.1$, 144.8, 133.3, 129.9, 129.5, 128.0, 120.7, 114.5, 70.6, 67.6, 29.1, 28.9, 25.6, 25.3, 21.7; elemental analysis calcd (%) for $C_{19}H_{24}O_4S$(348.46): C 65.49, H 6.94; found: C 65.44, H 6.98.

A solution of toluene-4-sulfonic acid 6-phenoxyhexyl ester (1.70 g, 4.88 mmol), phthalimide (2.15 g, 14.6 mmol, 3 equiv), and K_2CO_3 (3.03 g, 21.9 mmol, 4.5 equiv) in DMF (30 mL) was heated at 60–70 °C for 9 h. The mixture was concentrated under reduced pressure and the residue was taken up in CH_2Cl_2. The organic solution was washed with HCl (1N) solution, saturated $NaHCO_3$, and brine, dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by column chromatography (EtOAc/*n*-hexane/CH_2Cl_2 1:4:1) to give 2-(6-phenoxyhexyl)isoindole-1,3-dione (**3b**; 1.48 g, 94%) as a white solid. M.p. 62–64 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.85–7.82$ (m, 2H; Ar-H), 7.71–7.68 (m, 2H; Ar-H), 7.29–7.23 (m, 2H; Ar-H), 6.93–6.85 (m, 3H; Ar-H), 3.94 (t, $^3J(H,H) = 6.4$ Hz, 2H; $ArOCH_2$), 3.69 (t, $^3J(H,H) = 7.2$ Hz, 2H; NCH_2), 1.83–1.66 (m, 4H; CH_2), 1.57–1.37 (m, 4H; CH_2); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 168.6$, 159.2, 134.0, 132.3, 129.5, 123.3, 120.6, 114.6, 67.8, 38.1, 29.3, 28.7, 26.8, 25.8; IR (KBr): $\tilde{\nu} = 1702$ (C=O) cm^{-1}; elemental analysis calcd (%) for $C_{20}H_{21}NO_3$ (323.4): C 74.28, H 6.55, N 4.33; found: C 73.81, H 7.06, N 4.36.

A solution of **3b** (1.40 g, 4.33 mmol) and hydrazine hydrate (55% N_2H_4, 1.5 mL, excess) in ethanol (50 mL) was heated at reflux for 18 h, then cooled to room temperature, and filtered. The filtrate was concentrated, then taken up in CH_2Cl_2 (50 mL), washed with H_2O and brine, and dried over anhydrous $MgSO_4$, and concentrated. The resulting yellowish liquid of 6-phenoxyhexylamine was used in the next step without further purification (0.90 g). A solution of hexane-1,6-dioic acid bis(pentafluorophenyl) ester (0.59 g, 1.23 mmol) in dry CH_2Cl_2 (5 mL) was added under argon at 0 °C (ice-water bath) to a solution of 6-phenoxyhexylamine (0.60 g, 3.10 mmol, 2.5 equiv), Et_3N (0.69 mL, 4.95 mmol, 4 equiv), and 4-dimethylaminopyridine (DMAP) (0.15 g, 1.23 mmol, 1 equiv) in CH_2Cl_2 (10 mL). After stirring at room temperature for 4 h, the mixture was washed with HCl solution (1N), saturated $NaHCO_3$ solution, and brine, and then the mixture was dried over anhydrous $MgSO_4$. The product was purified by column chromatography (MeOH/CH_2Cl_2 1:10) to give hexane-1,6-dioic acid bis[(6-phenoxyhexyl)amide] **4b** (0.40 g, 65%) as a white solid. M.p.

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132–133 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.30-7.23$ (m, 4H; Ar-H), 6.95–6.86 (m, 6H; Ar-H), 5.66 (s, 2H; NH), 3.94 (t, $^3J(H,H) = 6.4$ Hz, 4H; OCH_2), 3.25 (m, 4H; NCH_2), 2.17 (br s, 4H; $C(=O)CH_2$), 1.77 (m, 4H; CH_2), 1.65 (br s, 4H; CH_2), 1.56–1.34 (m, 12H; CH_2); ^{13}C NMR (63 MHz, $CDCl_3$) $\delta = 172.8$, 159.2, 129.6, 120.7, 114.6, 67.8, 39.6, 36.3, 29.7, 29.3, 26.8, 25.9, 25.1; IR (KBr): $\tilde{\nu} = 3297$ (NH), 1636 (C=O) cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{44}N_2O_4$ (496.7): C 72.55, H 8.93, N, 5.64; found: C 72.57, H 8.92, N 5.61.

Hexane-1,6-dioic acid bis{[6-(3,5-di-*tert*-butylphenoxy)hexyl]amide} (4c): The compound **4c** was prepared by following the same procedures described for **4b** except 3,5-di-*tert*-butylphenol was used instead of phenol. M.p. 139 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.01$ (t, $^4J(H,H) = 1.5$ Hz, 2H; Ar-H), 6.75 (t, $^4J(H,H) = 1.5$ Hz, 4H; Ar-H), 5.62 (br s, 2H; NH), 3.95 (t, $^3J(H,H) = 6.4$ Hz, 4H; $ArOCH_2$), 3.26 (m, 4H; NCH_2), 2.19 (br s, 4H; $C(=O)CH_2$), 1.76 (m, 4H; CH_2), 1.66 (br s, 4H; CH_2), 1.56–1.48 (m, 8H; CH_2), 1.41 (m, 4H; CH_2), 1.30 (s, 18H; $C(CH_3)_3$); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 172.8$, 158.8, 152.3, 115.0, 108.9, 67.7, 39.6, 36.4, 35.1, 31.6, 29.8, 29.6, 26.9, 26.0, 25.1; IR (KBr): $\tilde{\nu} = 3302$ (NH), 1638 (C=O) cm^{-1}; elemental analysis calcd (%) for $C_{46}H_{76}N_2O_4$ (721.1): C 76.62, H 10.62, N 3.88; found: C 76.59, H 10.68, N 3.91.

Hexane-1,6-dioic acid bis{[6-(4-tritylphenoxy)hexyl]amide} (4d): The compound **4d** was prepared by following the same procedures described for **4b** but 4-tritylphenol and adipoyl chloride were used instead of phenol and hexane-1,6-dioic acid bis(pentafluorophenyl) ester, respectively. M.p. 158–159 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.24-7.14$ (m, 30H; Ar-H), 7.08 (d, $^3J(H,H) = 8.9$ Hz, 4H; Ar-H), 6.75 (d, $^3J(H,H) = 8.9$ Hz, 4H; Ar-H), 5.68 (s, 2H; NH), 3.91 (t, $^3J(H,H) = 6.3$ Hz, 4H; OCH_2), 3.24 (m, 4H; NCH_2), 2.17 (br s, 4H; $C(=O)CH_2$), 1.74 (m, 4H; CH_2), 1.63 (m, 4H; CH_2), 1.57–1.36 (m, 12H; CH_2); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta =$ 172.8, 157.1, 147.1, 138.9, 132.3, 131.2, 127.5, 126.0, 113.3, 67.7, 64.4, 39.6, 36.3, 29.7, 29.4, 26.8, 26.0, 25.1; IR (KBr): $\tilde{\nu} = 3295$ (NH), 1644 (C=O) cm^{-1}; elemental analysis calcd (%) for $C_{68}H_{72}N_2O_4$ (981.3): C 83.23, H 7.40, N 2.85; found: C 83.20, H 7.45, N, 2.87.

Hexane-1,6-dioic acid bis[(6-{4-[tris(4-*tert*-butylphenyl)methyl]phenoxy}-hexyl)amide] (4e): The compound **4e** was prepared by following the same procedures described for **4b** except 4-[tris(4-*tert*-butylphenyl)methylphenol was used instead of phenol. M.p. 216 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.24-7.20$ (m, 12H; Ar-H), 7.09–7.05 (m, 16H; Ar-H), 6.73 (d, $^3J(H,H) = 8.8$ Hz, 4H; Ar-H), 5.64 (s, 2H; NH), 3.91 (t, $^3J(H,H) = 6.3$ Hz, 4H; $ArOCH_2$), 3.24 (m, 4H; NCH_2), 2.17 (br s, 4H; $(C=O)CH_2$), 1.78–1.37 (m, 20H; CH_2), 1.29 (s, 54H; $C(CH_3)_3$); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta =$ 172.8, 157.0, 148.4, 144.3, 139.6, 132.4, 130.9, 124.2, 113.1, 67.7, 63.2, 39.6, 36.3, 34.4, 31.6, 29.8, 29.4, 26.9, 26.0, 25.1; IR (KBr): $\tilde{\nu} = 3421$ (NH), 1648 (C=O) cm^{-1}; elemental analysis calcd (%) for $C_{92}H_{120}N_2O_4$ (1318.0): C 83.84, H 9.18, N 2.13; found: C 83.84, H 9.30, N 2.17.

5-[6-(4-Tritylphenoxy)hexylcarbamoyl]pentanoic acid (7): A solution of benzyl alcohol (8.3 g, 77 mmol, 0.5 equiv) and Et_3N (15 mL, 110 mmol, 0.8 equiv) in dry CH_2Cl_2 (100 mL) was slowly added to a solution of adipoyl chloride (26 g, 142 mmol) in dry CH_2Cl_2 (50 mL) over 20 min at 0 °C (ice-water bath) under argon. After stirring for 2 h at room temperature, the mixture was washed with H_2O, and dried over anhydrous $MgSO_4$. The residue was purified with short silica column chromatography (CH_2Cl_2) to give **6** (6.6 g) which was contaminated by some impurities (≈5%), but used without further purification. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.35$ (s, 5H; Ar-H), 5.12 (s, 2H; $ArCH_2O$), 2.42–2.35 (m, 4H; $C(=O)CH_2$), 1.71–1.68 (m, 4H; CH_2). To a solution of **6** (2.2 g, 9.2 mmol, 2 equiv) and Et_3N (1.9 mL, 13.8 mmol, 3 equiv) in CH_2Cl_2 (15 mL) was added 2,2-dimethylpropionyl chloride (1.1 mL, 9.2 mmol, 2 equiv) at 0 °C. The mixture was stirred at room temperature for 1 h under argon, and 6-(4-tritylphenoxy)-hexylamine **5** (2.0 g, 4.6 mmol) was added to the solution. After stirring for an additional 1 h at room temperature, the mixture was washed with saturated $NaHCO_3$ and brine, and then dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by column chromatography ($MeOH/CH_2Cl_2$ 1:30) to give the desired amide (2.20 g, 73%) as a white solid, which was dissolved in EtOAc (50 mL) and MeOH (50 mL). A catalytic amount (≈0.3 g) of 5% Pd/C was added and the solution was stirred under a H_2 balloon for 1 h. The solution was then filtered through Celite and concentrated under reduced pressure to give **7** (1.67 g, 88%) as a white solid. M.p. 136–138 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 9.93$ (br, 1H; COOH), 7.23–7.15 (m, 15H; Ar-H), 7.09 (d, $^3J(H,H) = 8.8$ Hz, 2H; Ar-H), 6.76 (d, $^3J(H,H) = 8.8$ Hz, 2H; Ar-H), 5.74 (br s, 1H; NH), 3.92 (t, $^3J(H,H) = 6.3$ Hz, 2H; $ArOCH_2$), 3.25 (m, 2H; NCH_2), 2.38 (t, $^3J(H,H) = 6.3$ Hz, 2H; $C(=O)CH_2$), 2.19 (t, $^3J(H,H) = 6.7$ Hz, 2H; CH_2), 1.76–1.67 (m, 6H; CH_2), 1.53–1.27 (m, 6H; CH_2); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): $\delta = 178.3$, 173.1, 157.1, 147.1, 138.9, 132.3, 131.2, 127.5, 125.9, 113.3, 67.7, 63.4, 39.7, 36.3, 33.8, 29.6, 29.3, 26.8, 25.9, 25.1, 24.3; IR (KBr): $\tilde{\nu} = 3432$ (COOH), 1707 (C=O), 1623 (C=O) cm^{-1}; elemental analysis calcd (%) for $C_{37}H_{41}NO_4$ (563.7): C 78.83, H 7.33, N 2.48; found: C 78.86, H 7.46, N 2.50.

2-(2-{2-[4-(2-Methoxyethoxy)phenoxy]ethoxy}ethoxy)ethanol (8a): Compound **8a** was prepared by sequential coupling reactions of *p*-hydroquinone with approximately one equivalent of each toluene-4-sulfonic acid 2-methoxyethyl ester and tri(ethylene glycol) mono-*p*-tosylate. Reactions were heated at reflux in CH_3CN for 5–7 h in the presence of K_2CO_3 (3 equiv), and yields were 34% and 56% for the first and second steps, respectively. M.p. 35–37 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 6.79$ (s, 4H; Ar-H), 4.04–3.98 (m, 4H; OCH_2CH_2O), 3.78 (m, 2H; OCH_2CH_2O), 3.68–3.61 (m, 8H; OCH_2CH_2O), 3.55 (m, 2H; OCH_2CH_2O), 3.38 (s, 3H; OCH_3); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): $\delta = 153.1$, 153.0, 115.5, 72.5, 71.1, 70.7, 70.3, 69.8, 67.9, 67.8, 61.6, 59.1; IR (KBr): $\tilde{\nu} = 3367$ (OH), 2876 (CH_2-O-CH_2) cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{24}O_6$ (300.4): C 59.98, H 8.05; found: C 59.91, H 8.01.

2-(2-{2-[5-(2-Methoxyethoxy)naphthalen-1-yloxy]ethoxy}ethoxy)ethanol (8b): Compound **8b** was prepared from 1,5-dihydroxynaphthalene with approximately one equivalent each of toluene-4-sulfonic acid 2-methoxyethyl ester and tri(ethylene glycol) mono-*p*-tosylate. The mixture was heated at reflux in CH_3CN overnight (≈16 h) in the presence of K_2CO_3 (3 equiv), and yields were 37% and 83% for the first and second steps, respectively. M.p. 29–31 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.91-7.85$ (m, 2H; Ar-H), 7.39–7.32 (m, 2H; Ar-H), 6.85 (m, 2H; Ar-H), 4.32–4.27 (m, 4H; OCH_2CH_2O), 4.00 (m, 2H; OCH_2CH_2O), 3.89 (m, 2H; OCH_2CH_2O), 3.82 (m, 2H; OCH_2CH_2O), 3.79–3.69 (m, 4H; OCH_2-CH_2O), 3.62 (m, 2H; OCH_2CH_2O), 3.51 (s, 3H; OCH_3); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): $\delta = 154.5$, 154.4, 126.9, 126.8, 125.2, 114.8, 114.7, 105.8, 72.6, 71.2, 71.1, 70.6, 69.9, 68.0, 67.9, 61.9, 59.4; IR (KBr): $\tilde{\nu} = 3455$ (OH) cm^{-1}; elemental analysis calcd(%) for $C_{19}H_{26}O_6$ (350.4): C 65.13, H 7.48; found: C 65.15, H 7.51.

Hexane-1,6-dioic acid [2-(2-{2-[4-(2-methoxyethoxy)phenoxy]ethoxy}-ethoxy)ethyl]amide [6-(4-tritylphenoxy)hexyl]amide (10a): Amines **9a** and **9b** were prepared from the precursor alcohols **8a** and **8b**, according to the same procedures described for the conversion of hexane-1,6-diol into 6-phenoxyhexylamine. To a solution of carboxylic acid **7** (0.20 g, 0.35 mmol, 1.2 equiv) in dry CH_2Cl_2 (20 mL), trimethylacetyl chloride (0.034 mL, 0.28 mmol, 0.9 equiv), and Et_3N (0.10 mL, 0.72mmol, 2.4 equiv) were added. The solution was stirred under argon for 1 h at room temperature, and then amine **9a** (0.089 g, 0.30 mmol) was added. After stirring for 2 h at room temperature, the mixture was washed with saturated $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by column chromatography ($MeOH/CH_2Cl_2$ 1:15) to give **10a** (0.13 g, 51%) as a white solid. M.p. 99–101 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 7.23-7.17$ (m, 15H; Ar-H), 7.08 (d, $^3J(H,H) = 8.9$ Hz, 2H; Ar-H), 6.84 (s, 4H; Ar-H), 6.75 (d, $^3J(H,H) = 8.9$ Hz, 2H; Ar-H), 6.21 (br s, 1H; NH), 5.81 (br s, 1H; NH), 4.10–4.04 (m, 4H; OCH_2), 3.91 (t, $^3J(H,H) = 6.3$ Hz, 2H; $ArOCH_2$), 3.82 (t, $^3J(H,H) = 4.6$ Hz, 2H; OCH_2-CH_2O), 3.74–3.69 (m, 4H; OCH_2CH_2O), 3.65 (m, 2H; OCH_2CH_2O), 3.56 (t, ^3J (H,H) = 4.9 Hz, 2H; NCH_2CH_2O), 3.44 (br s, 5H; NCH_2, OCH_3), 3.24 (m, 2H; NCH_2), 2.14 (br s, 4H; $C(=O)CH_2$), 1.76 (m, 2H; CH_2), 1.61 (br s, 4H; CH_2), 1.55–1.37 (m, 6H; CH_2); ^{13}C NMR (125 MHz , $CDCl_3$): $\delta =$ 173.0, 172.8, 157.1, 153.4, 153.1, 147.2, 138.9, 132.3, 131.2, 127.5, 125.9, 115.7, 113.3, 71.3, 70.8, 70.3, 70.0, 69.9, 68.3, 68.0, 67.8, 64.4, 59.3, 40.0, 39.3, 36.4, 36.1, 29.7, 29.4, 26.8, 26.0, 25.3, 25.0; IR (KBr): $\tilde{\nu} = 3300$ (NH), 1640 (C=O) cm^{-1}; elemental analysis calcd (%) for $C_{52}H_{64}N_2O_8$ (845.1): C 73.91, H 7.63, N 3.31; found: C 73.95, H 7.60, N 3.36.

Hexane-1,6-dioic acid [2-(2-{2-[5-(2-methoxyethoxy)naphthalen-1-yloxy]-ethoxy}ethoxy)ethyl]amide [6-(4-tritylphenoxy)hexyl]amide (10b): The compound **10b** was prepared in 54% yield by following the same procedure described for **10a**. M.p. 88–90 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta =$ 7.87 (t, $^3J(H,H) = 8.6$ Hz, 2H; Ar-H), 7.34 (t, $^3J(H,H) = 8.0$ Hz, 2H; Ar-H), 7.24–7.17 (m, 15H; Ar-H), 7.08 (d, $^3J(H,H) = 8.9$ Hz, 2H; Ar-H), 6.84 (d, $^3J(H,H) = 7.6$ Hz, 2H; Ar-H), 6.75 (d, $^3J(H,H) = 8.9$ Hz, 2H; Ar-H), 6.08 (br s, 1H; NH), 5.73 (br s, 1H; NH), 4.32–4.26 (m, 4H; $ArOCH_2$), 3.99 (t, $^3J(H,H) = 4.6$ Hz, 2H; OCH_2CH_2O), 3.93–3.86 (m, 4H; $ArOCH_2$), 3.79

(m, 2H; OCH_2CH_2O), 3.67 (m, 2H; OCH_2CH_2O), 3.56 (t, ^3J(H,H) = 4.9 Hz, 2H; NCH_2CH_2O), 3.50 (s, 3H; OCH_3), 3.43 (m, 2H; NCH_2), 3.22 (m, 2H; NCH_2), 2.06–2.03 (m, 4H; $C(=O)CH_2$), 1.73 (m, 2H; CH_2), 1.50–1.34 (m, 10H; CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.9, 172.8, 157.1, 154.6, 154.4, 147.2, 138.9, 132.3, 131.2, 127.5, 127.0, 126.9, 126.0, 125.3, 125.2, 115.0, 114.6, 113.3, 106.0, 105.9, 71.3, 71.0, 70.5, 70.0, 69.9, 68.1, 68.0, 67.8, 64.4, 59.4, 39.5, 39.3, 36.3, 36.0, 29.7, 29.4, 26.8, 26.0, 25.2, 24.9; IR (KBr): $\tilde{\nu}$ = 3292 (NH), 1638 (C=O) cm^{-1}; elemental analysis calcd (%) for $C_{56}H_{66}N_2O_8$ (895.1): C 75.14, H 7.43, N 3.13; found: C 75.08, H 7.53, N 3.18.

Hexane-1,6-dioic acid [6-(4-tritylphenoxy)hexyl]amide (2-{2-[2-(4-{2-[2-(2-{5-[6-(4-tritylphenoxy)hexylcarbamoyl]pentanoylamino}ethoxy)ethoxy]-ethoxy}phenoxy)ethoxy]ethoxy}ethyl)amide (13a): Diamines **12a** and **12b** were prepared according to the same procedures that were described earlier for the preparation of monoamines **9a** and **9b** from *p*-hydroquinone and 1,5-dihydroxynaphthalene, respectively. To a solution of carboxylic acid **7** (0.30 g, 0.53 mmol, 3 equiv) in CH_2Cl_2 (20mL) was added 2,2-dimethylpropionyl chloride (0.065 mL, 0.53 mmol, 2.9 equiv) and Et_3N (0.10 mL, 0.72 mmol, 4 equiv). The mixture was stirred for 1 h under argon and diamine **12a** (0.066 g, 0.18 mmol) was added. After stirring for 1 h at room temperature, the mixture was washed with saturated $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, and concentrated. The residue was purified with column chromatography (MeOH/CH_2Cl_2 1:10) to give **13a** (0.10 g, 38%) as a white solid. M.p. 98–100 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 7.24–7.16 (m, 30H; Ar-H), 7.08 (d, ^3J(H,H) = 9.0 Hz, 4H; Ar-H), 6.83 (s, 4H; Ar-H), 6.75 (d, ^3J(H,H) = 9.0 Hz, 4H; Ar-H), 6.23 (brs, 2H; NH), 5.86 (brs, 2H; NH), 4.08 (m, 4H; $ArOCH_2$), 3.91 (t, ^3J(H,H) = 6.3 Hz, 4H; $ArOCH_2$), 3.82 (m, 4H; OCH_2CH_2O), 3.70 (m, 4H; OCH_2CH_2O), 3.64 (m, 4H; OCH_2CH_2O), 3.55 (t, ^3J(H,H) = 4.9 Hz, 4H; OCH_2CH_2O), 3.44 (m, 4H; NCH_2), 3.22 (m, 4H; NCH_2), 2.14 (brs, 8H; CH_2), 1.74 (m, 4H; CH_2), 1.61 (m, 8H; CH_2), 1.52–1.33 (m, 12H; CH_2); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): δ = 173.0, 172.8, 157.2, 153.2, 147.2, 138.9, 132.3, 131.3, 127.5, 126.0, 115.8, 113.3, 70.9, 70.4, 70.0, 69.9, 68.3, 67.8, 64.4, 39.6, 39.3, 36.4, 36.1, 29.7, 29.4, 26.9, 26.0, 25.3, 25.0; IR (KBr): $\tilde{\nu}$ = 3299 (NH), 1640 (C=O) cm^{-1}; elemental analysis calcd (%) for $C_{92}H_{110}N_4O_{12}$(1463.9): C 75.48, H 7.57, N 3.83; found: C 75.43, H 7.52, N 3.83.

Hexane-1,6-dioic acid [6-(4-tritylphenoxy)hexyl]amide (2-{2-[2-(5-{2-[2-(2-{5-[6-(4-tritylphenoxy)hexylcarbamoyl]pentanoylamino}ethoxy)ethoxy]-ethoxy}naphthalen-1-yloxy)ethoxy]ethoxy}ethyl)amide (13b): The compound **13b** was prepared in 63% yield by following the same procedure described for **10a**. M.p. 108–110 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 7.86 (d, ^3J(H,H) = 8.5 Hz, 2H; Ar-H), 7.34 (t, ^3J(H,H) = 8.0 Hz, 2H; Ar-H), 7.26–7.13 (m, 30H; Ar-H), 7.08 (d, ^3J(H,H) = 8.8 Hz; 4H; Ar-H), 6.85 (d, ^3J (H,H) = 7.5 Hz, 2H; Ar-H), 6.76 (d, ^3J(H,H) = 8.8 Hz, 4H; Ar-H), 6.09 (brs, 2H; NH), 5.80 (brs, 2H; NH), 4.30 (t, ^3J(H,H) = 4.7 Hz, 4H; $ArOCH_2$), 4.00 (t, ^3J(H,H) = 4.6 Hz, 4H; OCH_2CH_2O), 3.90 (t, ^3J(H,H) = 6.4 Hz, 4H; $ArOCH_2$), 3.78 (m, 4H; OCH_2CH_2O), 3.66 (m, 4H; OCH_2CH_2O), 3.55 (t, ^3J(H,H) = 5.0 Hz, 4H; OCH_2CH_2O), 3.41 (m, 4H; OCH_2CH_2O), 3.21 (m, 4H; NCH_2), 2.07–2.04 (m, 8H; CH_2), 1.80–1.72 (m, 4H; CH_2), 1.57–1.36 (m, 20H; CH_2); ^{13}C NMR (63 MHz, $CDCl_3$, 25 °C): δ = 172.9, 172.8, 157.2, 154.5, 147.2, 138.9, 132.3, 131.3, 127.5, 126.9, 126.0, 125.4, 114.8, 113.3, 106.0, 71.1, 70.5, 70.0, 69.9, 68.2, 67.8, 64.4, 39.6, 39.3, 36.4, 36.1, 29.7, 29.4, 26.9, 26.0, 25.2, 24.9; IR (KBr): $\tilde{\nu}$ = 3296 (NH), 1641 (C=O) cm^{-1}; elemental analysis calcd (%) for $C_{96}H_{112}N_4O_{12}$ (1513.9): C 76.16, H 7.46, N 3.70; found: C 76.16, H 7.48, N.3.71

Determination of binding constant (K_a, M^{-1}): Chloroform was stored over 4 Å molecular sieves, and filtered through basic alumina (Al_2O_3) prior to use. The $CDCl_3$ solutions of a 1:1 molar mixture of macrocycle **2** and threads **4c–e** were separately prepared in five NMR tubes, concentrations of which were 5.0, 2.0, 1.0, 0.5, and 0.2 mM. The ^{1}H NMR (500 MHz) spectrum of each solution was recorded at 25 °C, and the integration of well-separated amide NH peaks of both **2** and **4c–e** gave the ratios of the free components and the complex. The association constants reported were an average of ten values obtained for each combination of the macrocycle and the thread, and errors were within 20%.

2D-EXSY experiments:[16] The EXSY spectrum was recorded on a DRX-500 spectrometer at a given temperature. The concentration of each macrocycle and thread is 10–20 mM in $CDCl_3$ and molar ratios of two components are in the range of 0.7–1.5. The mixing time was 50–300 ms, and each of 128F_1 increments was the accumulation of 32 scans. Prior to Fourier transformation, the FIDs were multiplied by a 90° shifted square sine bell in F_1 and 60° shifted in F_2 domain. The data file was zero-filled, affording a spectrum of 2 × 256 K real data points. The rate constants (k) were calculated employing Equations (1)–(5) shown below, where I_{AB} and I_{BA} are cross peak intensities, I_{AA} and I_{BB} are diagonal peak intensities, and X_A, X_B are molar fractions of the free and complex which was determined by ^{1}H NMR integration.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \tag{1}$$

$$k = k_1 + k_{-1} \tag{2}$$

$$k = \frac{1}{\tau_m} \times \mathrm{In}\frac{r+1}{r-1} \tag{3}$$

$$r = 4X_aX_b\frac{(I_{AA}+I_{BB})}{(I_{AB}+I_{BA})} - (X_A - X_B)^2 \tag{4}$$

$$\Delta G^{+} = -RT\mathrm{In}\frac{kh}{k_bT} \tag{5}$$

(R = 1.9872 cal K^{-1} mol^{-1}, k_B = 3.2995 × 10^{-24} cal K^{-1}, h = 1.5836 × 10^{-34} cal s)

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