Self-Assembly of Novel [3]- and [2]Rotaxanes with Two Different Ring Components: Donor−Acceptor and Hydrogen Bonding Interactions and Molecular-Shuttling Behavior

Xin Zhao, Xi-Kui Jiang, Min Shi, Yi-Hua Yu, Wei Xia, and Zhan-Ting Li*

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

ztli@pub.sioc.ac.cn

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Three of the first kind of hetero[3]rotaxanes, which comprise one linear component and one neutral and one tetracationic ring component, have been assembled by using the intermolecular hydrogen bonding and donor−acceptor interactions. Three neutral [2]rotaxanes and three tetracationic [2]-rotaxanes have also been synthesized as intermediate products or for the sake of property comparison. The linear molecules are incorporated with two glycine subunits, for templating the formation of the neutral tetraamide cyclophane, and one or two hydroquinone subunits, for inducing the formation of the tetracationic cyclophane. Variable-temperature ^{1}H NMR investigation reveals that the shuttling behavior of the tetracationic ring component along the linear component is substantially influenced by the existence of the neutral ring component. The spatial repelling interaction of the neutral ring on the electron-deficient tetracationic ring simultaneously weakens the latter's "positioning" tendency at both electron-rich hydroquinone sites of the linear component. As a result, the activation energy associated with the shuttling process of the tetracationic ring between the two hydroquinone sites is remarkably reduced in comparison to that of the shuttling process of the corresponding neutral ring-free [2]rotaxanes. For the first time, the rotation of the dipyridinium subunit around the axis formed by the two methylene groups connecting them within the tetracationic cyclophane has been investigated by variable-temperature ^{1}H NMR spectroscopy and the associated kinetic data have also been successfully obtained. Furthermore, the UV−vis and fluorescent properties of the new [2]- and [3]rotaxanes have been studied. The results demonstrate that [3]rotaxanes with different ring components possess unique kinetic features that are not available in [3]rotaxanes with identical ring components.

Introduction

Rotaxanes are functional assemblies consisting of one linear dumbbell component and one or more ring components.[1] In the past decade, rotaxanes have increasingly attracted the attention of chemists because of their unique structural features and potential applications in materials science and molecular devices.[2] Several general approaches, including transition metal and organic ligand interaction, donor−acceptor interaction, intermolecular hydrogen bonding, and hydrophobic interaction, have been developed for efficient assembly of this kind of interlocked supramolecular system.[1,3]

One of the key features of rotaxane systems is the shuttling movement of the ring component along the linear component. Such dynamic processes are mainly affected by the noncovalent interactions between the recognition sites of the ring and linear components. Systematic investigation and efficient control of the dynamic processes are prerequisite for the future application of rotaxanes as molecular devices. In the past

(1) (a) Gibson, H. W.; Bheda, M. C.; Engen, P. T. *Prog. Polym. Sci.* **1994**, *19*, 843. (b) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725. (c) Jäger, R.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 930. (d) Chambron, J.-C.; Sauvage, J.-P. *Chem. Eur. J.* **1998**, *4*, 1362. (e) Nepogodiev, S. A.; Stoddart, J. P. *Chem. Rev.* **1998**, *98*, 1959. (f) *Molecular Catenanes, Rotaxanes and Knots*; Sauvage, J.-P., Dietrich-Buchecker, C.-O., Eds.; Wiley-VCH: Weinheim, 1999. (g) Leigh, D. A.; Murphy, A. *Chem. Ind. (London)* **1999**, 178. (h) Hubin, T. J.; Kolchinski, A. G.; Vance, A. L.; Busch, D. H. *Adv. Supramol. Chem.* **1999**, *5*, 237. (i) Breault, G. A.; Hunter, C. A.; Mayers, P. C. *Tetrahedron* **1999**, *55*, 5265. (j) Raymo, F. M.; Stoddart, J. F. *Chem. Rev.* **1999**, *99*, 1643. (k) Cantrill, S. J.; Pease, A. R.; Stoddart, J. F. *J. Chem. Soc., Dalton Trans.* **2000**, 3715. (l) Hubin, T. J.; Busch, D. H. *Coord. Chem. Rev.* **2000**, *200*, 5.

(2) (a) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515. (b) Ward, M. D. *Chem. Ind. (London)* **1997**, 640. (c) Balzani, V.; Gómez-López, M.; Stoddart, J. F. *Acc. Chem. Res.* **1998**, *31*, 405. (d) Sauvage, J.-P. *Acc. Chem. Res.* **1998**, *31*, 611. (e) Kaifer, A. E. *Acc. Chem. Res.* **1999**, *32*, 42. (f) Collier, C. P.; Wong, E. W.; Belohradsky, M.; Raymo, F. M.; Stoddart, J. F.; Kuekes, P. J.; Williams, R. S.; Heath, J. R. *Science* **1999**, *285*, 391.

(3) (a) Clegg, W.; Gimenez-Saiz, C.; Leigh, D. A.; Murphy, A.; Slawin, A. M. Z.; Teat, S. J. *J. Am. Chem. Soc.* **1999**, *121*, 4124. (b) Craig, M. R.; Claridge, T. D. W.; Hutchings, M. G.; Anderson, H. L. *Chem. Commun.* **1999**, 1251. (c) Easton, C. J.; Lincoln, S. F.; Meyer, A. G.; Onagi, H. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2501. (d) Fabicon, R. M.; Parvez, M.; Richey, H. G. *Organometallics* **1999**, *18*, 5163. (e) Baer, A. J.; Macartney, D. H. *Inorg. Chem.* **2000**, *39*, 1410. (f) Chichak, K.; Walsh, M. C.; Branda, N. R. *Chem. Commun.* **2000**, 847. (g) Wong, E. W.; Collier, C. P.; Behloradsky, M.; Raymo, F. M.; Stoddart, J. F.; Heath, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 5831. (h) Buston, J. E. H.; Young, J. R.; Anderson, H. L. *Chem. Commun.* **2000**, 905. (i) Reuter, C.; Pawlitzki, G.; Worsdorfer, U.; Plevoets, M.; Mohry, A.; Kubota, T.; Okamoto, Y.; Vögtle, F. *Eur. J. Org. Chem.* **2000**, 3059. (j) Damgärd, D.; Nielsen, M. B.; Lau, J.; Jensen, K. B.; Zubarev, R.; Levillain, E.; Becher, J. *J. Mater. Chem.* **2000**, *10*, 2249. (k) Loeb, S. J.; Wisner, J. A. *Chem. Commun.* **2000**, 1939. (l) Hoshino, T.; Miyauchi, M.; Kawaguchi, Y.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2000**, *122*, 9876. (m) Jeppesen, J. O.; Perkins, J.; Becher, J.; Stoddart, J. F. *Org. Lett.* **2000**, *2*, 3547. (n) Shukla, R.; Deetz, M. J.; Smith, B. D. *Chem. Commun.* **2000**, 2397. (o) Linke, M.; Chambron, S. C.; Heitz, V.; Sauvage, S. P.; Encinas, S.; Barigelletti, F.; Flamigni, L. *J. Am. Chem. Soc.* **2000**, *122*, 11834.

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decade, noncovalent interactions in a variety of [2]-rotaxane systems have been extensively investigated. Several efficient approaches have been developed to control the shuttling movement of the ring component between the different recognition sites within the linear component.[1,4] However, there have not been systematic studies of the noncovalent interactions within more complicated [3]rotaxanes. One possible reason is that all the [3]rotaxanes presently reported consist of one linear component and two identical ring components, and there is no efficient method available yet to differentiate the two identical interactions of the rings with the linear component within these homo[3]rotaxanes.

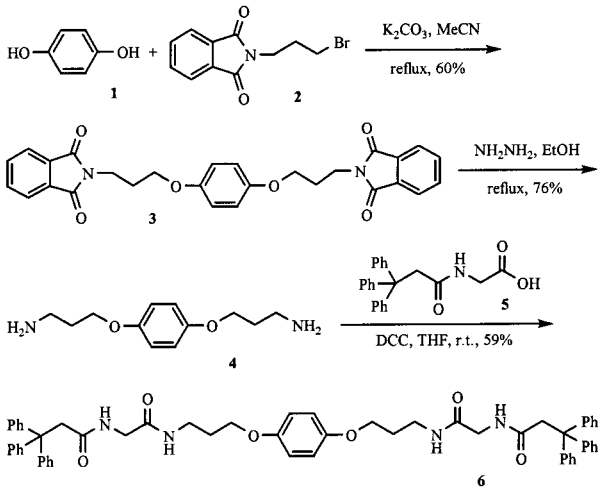
We have recently initiated a project to explore the assembling methodology of rotaxanes comprising rings with different structures and recognition sites. Such rotaxanes not only represent one new kind of supramolecular structure but also are expected to be useful as new models to investigate noncovalent interactions within more complicated interlocked systems. One simple approach would be to introduce two kinds of recognition sites into one linear templating molecule and to assemble [3]rotaxanes by stepwise induction of formations of two different ring components. Since the intermolecular donor−acceptor and hydrogen bonding interaction principles have been well-established for the efficient assembly of various rotaxanes,[5,6] we decided to synthesize new [3]rotaxanes by combining these two principles into one system. In this paper, we report self-assembly, characterizations, and new spectroscopic properties of three hetero[3]rotaxanes and six [2]rotaxanes.

Results and Discussion

Synthesis and Self-Assembly. We chose the so-called "clipping" strategy[1b] to assemble new [3]rotaxanes with two different ring components. Therefore, both hydroquinone and glycine moieties are incorporated into the dumbbell components. They are expected to template the formations of the tetracationic macrocycle and the neutral tetraamide macrocycle, respectively.[5,6] Three dumbbell molecules with different numbers of recognition sites or spacers of different lengths have been prepared.

The first dumbbell molecule **6**, with one hydroquinone and two glycine subunits, was synthesized as outlined in Scheme 1. Coupling of hydroquinone **1** with 2 equiv of bromide **2** in refluxing acetonitrile with potassium carbonate as a base gave compound **3**, which was deprotected with hydrazine in hot ethanol to afford diamine **4**. Treatment of **4** and acid **5** with the coupling reagent DCC in tetrahydrofuran led to the formation of compound **6**.

Scheme 1



Through the use of a similar method, linear molecules **11a** and **11b**, both possessing two hydroquinone and two glycine subunits, have been prepared, as shown in Scheme 2. Thus, compounds **9a** and **9b** were obtained, from the reaction of diol **7** and bromide **2** or **8**, in 83 and 62% yields, respectively. Deprotection of **9a** and **9b** with hydrazine generated **10a** and **10b**, respectively, which then reacted with **5** in the presence of DCC, to afford compounds **11a** and **11b**, respectively. All three dumbbell molecules **6**, **11a**, and **11b** have a triphenylmethyl group as the stopper. CPK modeling indicates that its size is large enough so that both tetracationic and neutral tetraamide macrocycles will not dethread through it.

With compound **6** as the template, two [2]rotaxanes and one [3]rotaxane have been assembled, as shown in Scheme 3. Thus, treatment of **6** with dicationic salt **12**·$2PF_6$ and dibromide **13** in acetonitrile at room temperature for 10 days gave tetracationic [2]rotaxane **14**·4Cl in 20% yield after column chromatography, whereas treatment of **6** with neutral 1,3-phthaloyl dichloride **15** and diamine **16** in chloroform at room temperature led to the formation of neutral [2]rotaxane **17** in 19% yield. Through the use of [2]rotaxane **17** as the template, [3]-rotaxane **18**·4Cl was assembled in a higher yield (31%) from the reaction of **12**·$2PF_6$ and dibromide **13**. It is obviously impossible to prepare **18**·4Cl with **14**·4Cl as the template, since the tetracationic [2]rotaxane **14**·4Cl is insoluble in chloroform, the suitable solvent for intermolecular hydrogen bonding-promoted assembly.

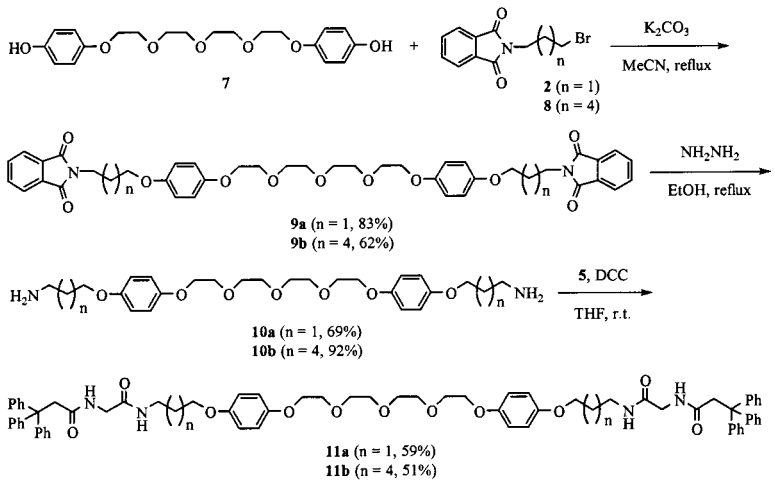
Under similar reaction conditions, another four [2]-rotaxanes (**19a**·4Cl, **19b**·$4PF_6$, **20a**, **20b**) and two [3]-rotaxanes (**21a**·4Cl, **21b**·4Cl) were synthesized, starting from template **11a** or **11b** (Scheme 4). Thus, the reaction of **12**·$2PF_6$ with **13** in the presence of **11a** or **11b** afforded [2]rotaxane **19a**·4Cl in 36% yield and **19b**·$4PF_6$ (after ionic exchange with ammonium hexafluorophosphate) in 27% yield after column chromatography. The reactions of **15** with **16** in the presence of **11a** or **11b** afforded [2]-rotaxanes **20a** and **20b** in 18 and 19% yields, respectively. Finally, [3]rotaxanes **21a**·4Cl and **21b**·4Cl were assembled in 54 and 47% yields, respectively, by treating [2]rotaxanes **20a** or **20b** with **12**·$2PF_6$ and **13** in acetonitrile. Although the linear compounds **11a** and **11b** were also designed with the aim of assembling new [3]-rotaxanes with two neutral rings and then [4]rotaxanes with two neutral and one tetracationic rings, no such [3]-

(4) (a) Murakami, H.; Kawabuchi, A.; Kotoo, K.; Kunitake, M.; Nakashima, M. *J. Am. Chem. Soc.* **1997**, *119*, 7605. (b) Ashton, P. R.; Ballardini, R.; Balzani, V.; Baxter, I.; Credi, A.; Fyfe, M. C. T.; Gandolfi, M. T.; Gómez-López, M.; Martínez-Díaz, M.-V.; Piersanti, A.; Spencer, N.; Stoddart, J. F.; Venturi, M.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1998**, *120*, 11932. (c) Leigh, D. A.; Troisi, A.; Zerbetto. *Angew. Chem., Int. Ed.* **2000**, *39*, 350. (d) Rowan, S. J.; Stoddart, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 164. (e) Jimenez, M. C.; Dietrich-Buchecker, C.; Sauvage, J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3284.

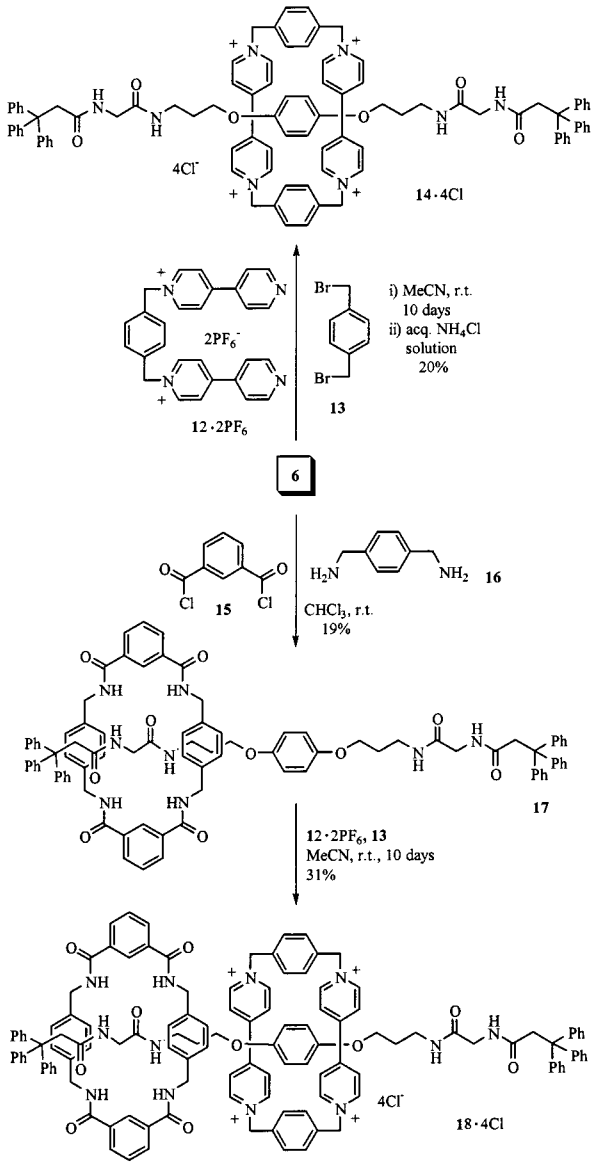
(5) Anelli, P. L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, M. T.; Goodmow, T. T.; Kaifer, A. E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Redington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *J. Am. Chem. Soc.* **1992**, *114*, 193.

(6) (a) Johnston, A. G.; Leigh, D. A.; Pritchard, R. J.; Deegan, M. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1209. (b) Johnston, A. G.; Leigh, D. A.; Nezhat, L.; Smart, J. P.; Deegan, M. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1212.

Scheme 2



Scheme 3



rotaxanes were detected from the two above-mentioned reactions to generate [2]rotaxanes **20a** and **20b**.

Although it is expected that the neutral macrocyclic component in [2]rotaxanes **17**, **20a**, and **20b** would impose spatial hindrance over the formation of the tetracationic cyclophane during the assembly of [3]-rotaxanes **18**·4Cl, **21a**·4Cl, and **21b**·4Cl, respectively, the yields of all three [3]rotaxanes **18**·4Cl, **21a**·4Cl, and **21b**·4Cl are remarkably higher than those of the corresponding [2]rotaxanes **14**·4Cl, **19a**·4Cl, and **19b**·4PF_6. We attribute this result to the fact that all neutral [2]-rotaxanes **17**, **20a**, and **20b** have better solubilities in acetonitrile than the simple dumbbell molecules **6**, **11a**, and **11b**. Therefore, the assembly of the [3]rotaxanes could be carried out at a higher concentration of starting materials, which was favorable to the formation of [3]-rotaxanes in such three-molecule assembling systems.

(Dynamic) ^{1}H NMR Spectroscopy and Molecular-Shuttling Properties. The structures of the [2]- and [3]-rotaxanes are characterized by ^{1}H NMR spectra. As expected, both the tetracationic [2]rotaxanes **19a**·4Cl and **19b**·4PF_6 and the neutral [2]rotaxanes **20a** and **20b** display temperature-dependent behavior. The free energies of activation for the shuttling processes of the ring components in these [2]rotaxanes are obtained on the basis of variable-temperature ^{1}H NMR data, according to the coalescence method (shown in Table 1).[7] The $\Delta G^{\ddagger}$ values of **20a** and **20b** are comparable to those reported for other similar [2]rotaxanes in which the glycine moieties are connected by linear aliphatic spacers, implying that the hydroquinone unit in the present study does not impose an important influence on the shuttling behavior.[8,9] The signal of the hydroquinone protons of [2]-rotaxane **14**·4Cl shifts upfield remarkably to 3.36 ppm (compared to the value of 6.80 ppm in compound **6**) as a result of the shielding of the dipyridinium units of the tetracationic cyclophane. However, a variable-temperature ^{1}H NMR study of **14**·4Cl does not reveal shuttling behavior for this [2]rotaxane, indicating that there is no substantial interaction between the glycine units of the linear component and the dipyridinium units of the cyclophane. No shuttling behavior was observed for

(7) The coalescence method (Sandstroom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; Chapter 6) uses the expression $K_c = \pi(\Delta\nu)/2^{1/2}$ to approximate the rotation rate at the coalescence temperature T_c, where $\Delta\nu$ is the limiting chemical shift difference (hertz) between coalescing signals in the absence of exchange. The free energy of activation $\Delta G^{\ddagger}$ was then determined with the Eyring equation.

(8) Lane, A. S.; Leigh, D. A.; Murphy, A. *J. Am. Chem. Soc.* **1997**, *119*, 11092.

(9) Leigh, D. A.; Murphy, A.; Smart, J. P.; Slawin, A. M. Z. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 728.

Scheme 4

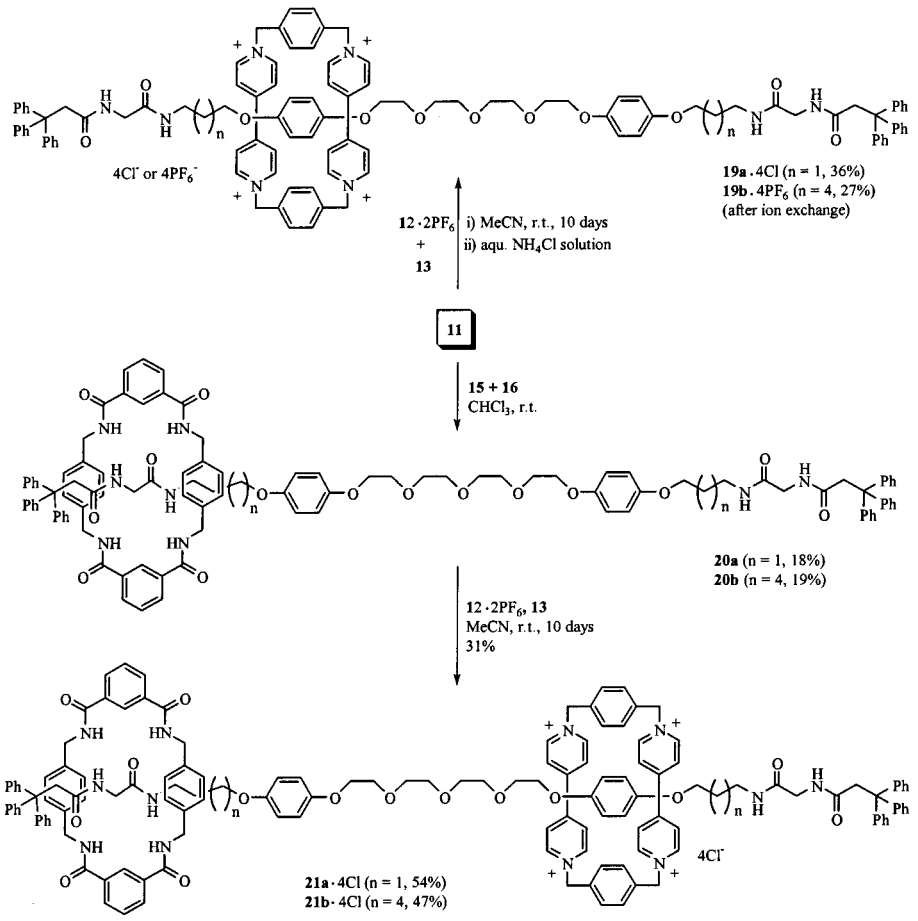


Table 1. Kinetic and Thermodynamic Parameters Associated with [2]Rotaxanes Based on the Temperature-Dependent ^{1}H NMR Method

rotaxane	probe	$\Delta\nu$ (Hz)[a]	k_c (s^{-1})	T_c (K)	$\Delta G^{\ddagger}$ (kcal^{-1} mol^{-1})	solvent
19a·4Cl	α-CH[b]	48	107	275	13.7	CD_3OD
19a·4Cl	β-CH[c]	75	167	284	13.8	CD_3OD
19a·4Cl	OC_6H_4O[d]	1224	2726	295	12.7	CD_3OD
19a·4Cl	$CH_2CH_2CH_2$	91	203	284	13.7	CD_3OD
19a·4Cl	NCH_2[e]	31	69	272	13.7	CD_3OD
19b·4PF_6	α-CH[b]	41	91	255	12.7	CD_3OD
19b·4PF_6	β-CH[c]	70	155	260	12.7	CD_3OD
19b·4PF_6	OC_6H_4O[d]	1180	2628	276	12.0	CD_3OD
19b·4PF_6	$CH_2C_6H_4$	38	85	250	12.2	CD_3OD
20a	$NHCH_2CH_2$	201	478	245	11.5	$CDCl_3$
20b	$NHCH_2CH_2$	193	430	250	11.7	$CDCl_3$

[a] With 10% errors. [b] CH α to the pyridine N of the tetracationic ring. [c] CH β to the pyridine N of the tetracationic ring. [d] Calculated from the average value of the doublet peaks. [e] Protons relating to the methylene groups of the tetracationic ring.

neutral [2]rotaxane **17** within the temperature range from 210 to 300 K, probably because the linker connecting the two glycine moieties of the linear component is relatively short so that selective "positioning" of the ring component to the glycine moiety would need a lower temperature. In other words, the shuttling process for **17** might be too fast to be detected within the investigated temperature range.

[3]Rotaxanes **18**·4Cl, **21a**·4Cl, and **21b**·4Cl comprise two different ring components. Consequently, all the previously symmetric functional groups of the three components, except the phthalic diamide aromatics of the neutral cyclophane, become asymmetric in their chemical environments. The ^{1}H NMR signals of **18**·4Cl and **21b**·4Cl have been assigned completely on the basis of 2D NOESY, DQCOSY, and TOCSY techniques. Comparison of their chemical shift values with those of the corresponding symmetric tetraamide cyclophane-free [2]rotaxanes **14**·4Cl and **19b**·4Cl reveals the influence of the neutral cyclophane over the linear component proton signals. All the proton signals of the two aliphatic spacers shift upfield remarkably, indicating the additional shielding effect of the neutral cyclophane in the [3]rotaxanes. A number of NOE interactions are also observed between the ring and linear component protons. However, such NOEs cannot be observed for the tetracationic [2]rotaxanes.

Variable-temperature ^{1}H NMR spectroscopy is used to investigate the possible kinetic processes of different moieties of these [3]rotaxanes. It is found that, although the methylene protons of the neutral cyclophanes of all three [3]rotaxanes exhibit two sets of doublets, the xylene benzene protons always display only one singlet within the investigated temperature range from 210 to 400 K. This observation indicates that, in the neutral cyclophane, the benzene units always revolve quickly around the axis formed by the two amide-substituted methylene groups on the ^{1}H NMR time scale.

The ^{1}H NMR spectra of the tetracationic ring protons of [3]rotaxanes **18**·4Cl, **21a**·4Cl, and **21b**·4Cl display a more complicated temperature dependence. At increased temperatures, both the α- and β-protons of the dipyridinium subunits of the tetracationic cyclophane of all [3]rotaxanes **18**·4Cl, **21a**·4Cl, and **21b**·4Cl in DMSO-d_6

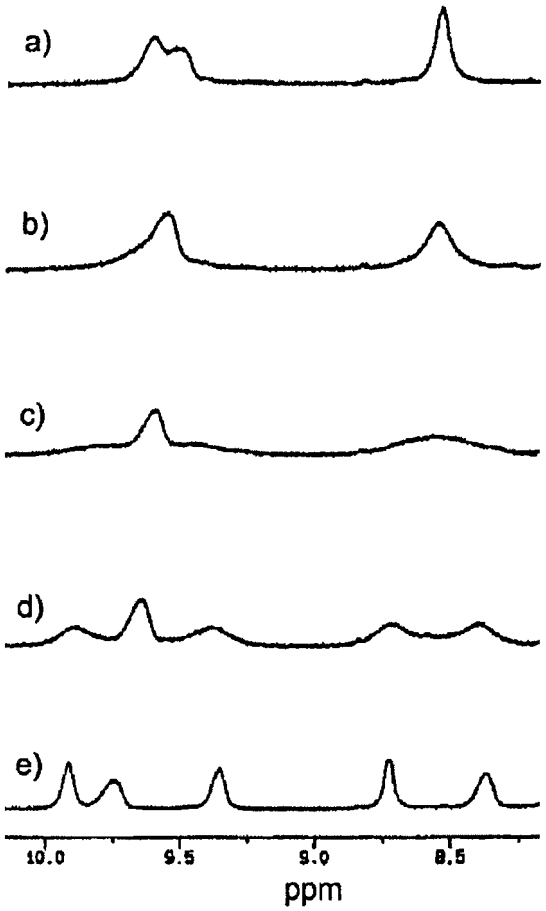


Figure 1. Partial variable-temperature ^{1}H NMR spectra (400 MHz, DMSO-d_6) of **21b**·4Cl, highlighting that the α-proton singlet (9.46 ppm) and β-proton singlet (8.43 ppm) of the pyridine (a) at 355 K gradually split into two singlets at the reduced temperatures (b) 345, (c) 335, (d) 325, and (e) 300 K.

Table 2. Kinetic and Thermodynamic Parameters Associated with the Rotation of the Dipyridinium Units around the Two Connectin Methylenes in [3]Rotaxanes Based on the Temperature-Dependent ^{1}H NMR Method

rotaxane	probe[a]	$\Delta\nu$ (Hz)[b]	k_c (s^{-1})	T_c (K)	$\Delta G^{\ddagger}$ ($kcal^{-1}\ mol^{-1}$)	solvent
18·4Cl	α-CH	236	526	295	13.7	DMSO-d_6
18·4Cl	β-CH	170	379	291	13.7	DMSO-d_6
21a·4Cl	α-CH	122	271	298	14.2	CD_3OD
21a·4Cl	β-CH	104	232	294	14.1	CD_3OD
21a·4Cl	α-CH	124	276	318	15.2	DMSO-d_6
21a·4Cl	β-CH	47	105	305	15.2	DMSO-d_6
21b·4Cl	α-CH	199	443	335	15.7	DMSO-d_6
21b·4Cl	β-CH	104	232	328	15.8	DMSO-d_6

[a] The pyridine CHs of the tetracationic ring. [b] With 10% errors.

exhibit one set of doublets, implying a fast revolving of the dipyridinium subunits around the axis of the two methylene groups connecting them on the ^{1}H NMR time scale. However, both the α- and β-proton signals gradually broaden and split into two separate signals at low temperatures, as shown in Figure 1 for [3]rotaxane **21b**·4Cl. The corresponding values of activation energy $\Delta G^{\ddagger}$ have been obtained by using the coalescence method and are listed in Table 2. In principle, such a rotation of the dipyridinium subunits can occur in any rotaxane systems comprising the tetracationic cyclophane. However, to our knowledge, this result represents the first quantitative measurement of the activation energy of this important

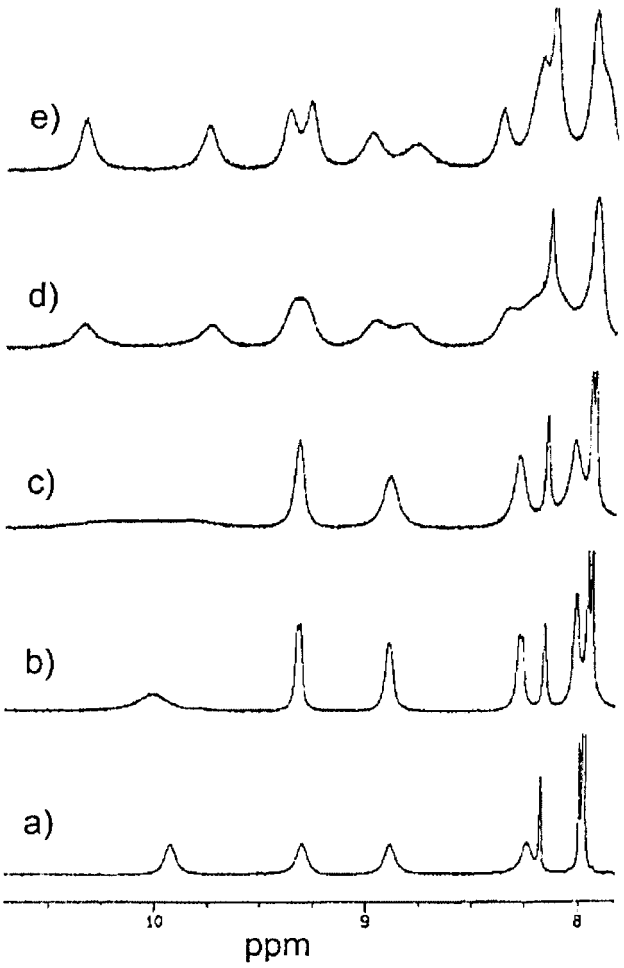


Figure 2. Partial variable-temperature ^{1}H NMR spectra (400 MHz, CD_3OD) of **21b**·4Cl, highlighting that the two α-proton signals (9.82, 9.21 ppm) and β-proton signals (8.84, 8.25 ppm) of the pyridine gradually split (a) at 300 K into two singlets at the reduced temperatures (b) 240, (c) 230, (d) 220, and (e) 210 K.

kinetic process in rotaxane systems. Although it is also found that the xylene benzene proton signals of these [3]-rotaxanes broaden gradually with decreases in temperature, no obvious coalescence temperature has been observed.

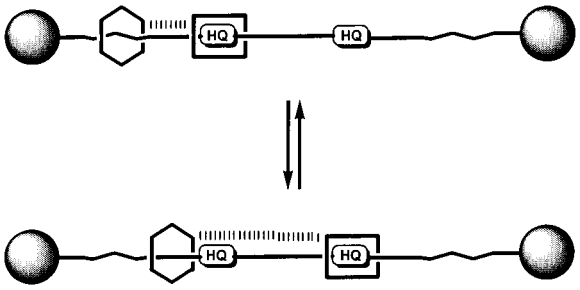
A variable-temperature ^{1}H NMR study also reveals that the tetracationic cyclophanes of the hetero[3]-rotaxanes **21a**·4Cl and **21b**·4Cl can display shuttling behavior at reduced temperatures. The direct evidence comes from the observation that, at sufficiently low temperatures, the four distinct signals mentioned above for the dipyridinium protons (Figure 1) of the tetracationic cyclophane broaden gradually and finally split into two separate signals (as can be seen in Figure 2 for **21b**·4Cl), clearly suggesting that not only has the rotation of the dipyridinium subunits around the axis of the two connecting methylene groups been stopped but the exchanging process of the tetracationic cyclophanes between the two hydroquinone units of the linear component has slowed and occurs at a rate lower than the ^{1}H NMR time scale. Under similar measuring conditions, no further splitting can be observed for the dipyridinium protons of [3]rotaxane **18**·4Cl. Since **18**·4Cl has only one hydroquinone in the linear component, this observation may be considered as indirect evidence to support the

Table 3. Data Associated with [3]Rotaxanes Associated with the Shuttling Behavior of the Tetracationic Cyclophane in [3]Rotaxanes 21a·4Cl and 21b·4Cl Based on the Temperature-Dependent ^{1}H NMR Method

rotaxane	probe[a]	$\Delta\nu$ (Hz)[b]	k_c (s^{-1})	T_c (K)	$\Delta G^{\ddagger}$ ($kcal^{-1}\ mol^{-1}$)	solvent
21a·4Cl	α-CH	120	267	213	10.2	CD_3OD
21b·4Cl	α-CH[c]	171	382	230	10.8	CD_3OD
21b·4Cl	α-CH[c]	34	76	212	10.7	CD_3OD
21b·4Cl	*β*-CH	69	153	328	10.5	CD_3OD

[a] The pyridine CHs of the tetracationic ring. [b] With 10% errors. [c] We are not able to differentiate the two sets of signals from each other.

Scheme 5[a]



[a] The neutral cyclophane (represented by the hexagon) always imposes a repelling interaction on the tetracationic cyclophane (represented by the tetragon), regardless of the latter's orientation over either of the two hydroquinones of the linear component in hetero[3]rotaxanes **21a**·4Cl and **21b**·4Cl. There are no intermolecular hydrogen bonding interactions between the glycine moiety and the neutral cyclophane in the polar solvent MeOH-d_4. The shuttling movement of the neutral cyclophane should have a much lower hindrance energy than that of the tetracationic cyclophane.

molecular-shuttling feature of [3]rotaxanes **21a**·4Cl and **21b**·4Cl. The $\Delta G^{\ddagger}$ values for the shuttling processes of the tetracationic cyclophanes of [3]rotaxanes **21a**·4Cl and **21b**·4Cl have also been determined with the coalescence method and are listed in Table 3. It can be found that the activation energy values of the shuttling processes of the hetero[3]rotaxanes are remarkably lower that those observed in the corresponding symmetric [2]rotaxanes, as shown in Table 1. This observation may indicate that the existence of the neutral tetraamide cyclophane simultaneously reduces the donor−acceptor interactions of the tetracationic cyclophane with the two hydroquinone moieties of the linear component. This result can be rationalized on the basis of the following considerations. It is reasonable to assume that the shuttling movement of the neutral cyclophane along the linear component is much quicker than that of the tetracationic cyclophane because of the lack of efficient interactions between the former cyclophane with the linear component. Therefore, the neutral cyclophane can impose an important spatial repelling interaction over the tetracationic cyclophane regardless of the latter's location along the linear component and, as a result, make it more difficult for the tetracationic cyclophane to be positioned to both the hydroquinone moieties of the linear component, as shown in Scheme 5. No shuttling behavior of the neutral ring component between the glycine subunits is observed for these [3]rotaxanes within the investigated temperature range.

Absorption Spectra and Luminescence Properties. Since there have not been similar rotaxane structures reported in the literature, the UV−vis properties of all the [2]- and [3]rotaxanes were investigated. A summary of their absorption data is presented in Table 4. All the experiments were carried out in methanol solution. The absorption bands observed for **6**, **11a**, and **11b**, all with maxima at 289 nm, are attributed to the hydroquinone units. Both **11a** and **11b** have an ϵ value about 2 times higher than that of **6** as a result of the existence of two hydroquinone units in these two compounds. The neutral [2]rotaxanes **17**, **20a**, and **20b** exhibit maximum absorption bands for the hydroquinone units, all at 287 nm with intensities similar to those of compounds **6**, **11a**, and **11b**, indicating that threading of the neutral cyclophane through these linear molecules does not impose an important effect on the hydroquinone units. The intense absorption bands observed for all the ionic [2]- and [3]rotaxanes with a maximum at about 262 nm are attributable to the bipyridinium units of the tetracationic cyclophane.[5] The molar absorption coefficients ϵ of the charge-transfer complexes in both [2]-rotaxane **14**·4Cl and [3]rotaxane **18**·4Cl are obviously lower than those of other tetracationic [2]- and [3]-rotaxanes (Table 4), not only reflecting the fact that the linear molecule **6** has only one hydroquinone unit but also suggesting that the tetracationic cyclophane in both **19a,b**·4Cl and **21a,b**·4Cl interacts with the two hydroquinone units, presumably for the linear components in a folded structure.

Excitation of the maximum absorption bands at 289 nm for the three linear molecules **6**, **11a**, and **11b** leads to the formation of emission bands with a maximum at 320 nm. With the same excitation light, similar emission bands are also observed for the neutral [2]rotaxanes **17**, **20a**, and **20b** at 322, 319, and 322 nm, respectively. However, the emission intensity of these [2]rotaxanes is only about 10% of that of the corresponding linear precursor molecules under the same measurement conditions. We attributed this remarkable quenching effect to the weak interaction between the excited hydroquinone and the neutral cyclophane. As expected, under similar conditions, no emission is observed for all the hydroquinone units of the tetracationic [2]- and [3]rotaxanes, reflecting the efficient quenching of the charge-transfer interactions.[5]

Conclusions

We have for the first time reported one general strategy for the efficient assembly of [3]rotaxanes comprising neutral and tetracationic ring components by utilizing the principles of intermolecular hydrogen bonding and donor−acceptor interactions. This new kind of hetero[3]-rotaxane exhibits more complicated ^{1}H NMR features because of its structural asymmetry. One of the ring components, the tetracationic ring, displays shuttling behavior, which can be revealed by variable-temperature ^{1}H NMR spectroscopy. The rotation of the subunits of the ring component around the axis of the two subunits connecting them can also be investigated by variable-temperature ^{1}H NMR spectroscopy. These results demonstrate that [3]rotaxanes of different ring components are useful models for the investigation of noncovalent interactions of different components in interlocked systems. Since the efficient assembly of interlocked supramolecular systems by means of other noncovalent interactions has now been well accomplished, it is expected that more new hetero[3]rotaxanes can be syn-

Table 4. Maximum and Charge-Transfer Absorptions of the Templates and Rotaxanes, Recorded in Methanol at Ambient Temperature

compound	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	compound	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	λ_{CT} (nm)	ϵ (M^{-1} cm^{-1})
6	289	2810	**14**·4Cl	261	26 950	466	300
11a	289	5090	**19a**·4Cl	263	31 730	463	700
11b	289	4820	**19b**·4PF_6	263	33 480	464	580
17	287	2810	**18**·4Cl	262	36 010	471	420
20a	287	5640	**21a**·4Cl	262	35 520	465	600
20b	287	4820	**21b**·4Cl	262	36 750	467	750

thesized in the future, which should display new unique structural and kinetic features.

Experimental Section

Methods and Materials. Melting points are uncorrected. ^{1}H NMR spectra were recorded on a 300, 400, or 600 MHz spectrometer with Me_4Si as the internal standard. Mass spectra were recorded in EI or ESI mode. Elemental analysis was carried out at the SIOC analytical center. All fluorescence measurements were made using a Perking Elmer LS 50B luminescence spectrometer at 25 °C. Absorption spectra were recorded at room temperature (25 °C) with a Perkin-Elmer lambda 5 spectrophotometer. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. The solvents have been purified by standard procedures before use.

1,4-Di(3-phthalimidoproxy)benzene 3. A suspension of hydroquinone **1** (5.5 g, 0.05 mol), *N*-(3-bromopropyl)phthalimide **2** (26.8 g, 0.10 mol), and potassium carbonate (27.6 g, 0.20 mol) in acetonitrile (500 mL) in a 1000 mL of flask was heated under refluxing for 48 h. After cooling to room temperature, the reaction mixture was filtered. The filtrate was concentrated, and the resulting residue was triturated with 500 mL of dichloromethane. The organic solution was washed with 2 M sodium carbonate solution (2 × 50 mL×), water (50 mL), and brine (50 mL) and dried over $MgSO_4$. After the solvent was removed under reduced pressure, the resulting residue was purified by chromatography (silica gel, CH_2Cl_2 as the eluent). Compound **3** (14.5 g, 60%) was obtained as a colorless solid. Mp: 170−171 °C. ^{1}H NMR ($CDCl_3$): δ 7.89−7.79 (m, 4 H), 7.74−7.65 (m, 4 H), 6.70 (s, 4 H), 3.96 (t, 4 H), 3.90 (t, 4 H), 2.15 (m, 4 H). MS (EI): *m*/*z* 484 (M^+). Anal. Calcd for $C_{28}H_{24}O_6N_2$·0.25H_2O: C, 68.80; H, 4.85; N, 5.63. Found: C, 68.77; H, 5.06; N, 5.73.

1,4-Di(3-aminopropoxy)benzene 4. Compound **3** (9.68 g, 0.02 mol) was dissolved in hot ethanol (150 mL), and aqueous hydrazine hydrate (3 mL, 85%) was added. The reaction mixture was heated under reflux for 1.5 h. After the mixture was cooled, water (25 mL) was added and the suspension was concentrated to about 30 mL under reduced pressure. Hydrogen chloride solution (1 N) was added dropwise until no solid was generated. The precipitate was filtered off, and the filtrate was basified by 1 N NaOH solution. The resulting white precipitate was filtered and washed with water completely and then dried to give 3.40 g of compound **4** (76%) as a pale white solid. Mp: 110−111 °C. ^{1}H NMR (DMSO-d_6): δ 6.89 (s, 4 H), 4.00 (t, 4 H), 3.25 (br, 4 H), 2.56 (t, 4 H), 1.82−1.78 (m, 4 H). MS (EI): *m*/*z* 224 (M^+). Anal. Calcd for $C_{12}H_{20}O_2N_2$·0.25H_2O: C, 62.71; H, 8.69; N, 11.85. Found: C, 62.98; H, 9.05; N, 12.23.

Compound 5. To a solution of glycine ethyl ester hydrochloride (4.60 g, 33 mmol) and Et_3N (20 mL) in dry CH_2Cl_2 (200 mL) was added a solution of 3,3,3-triphenylpropionic chloride[10] (10.6 g, 33 mmol) in dry CH_2Cl_2 (60 mL) with stirring at room temperature for 1 h. The solution was stirred for another 24 h, and the solvent was removed under reduced pressure. The resulting residue was triturated with CH_2Cl_2 (200 mL) again, and the solution was washed with saturated NH_4Cl solution (50 mL), water (50 mL), and brine (50 mL) and then dried over anhydrous sodium sulfate. After the solvent was evaporated under reduced pressure, the residue was purified by chromatography (silica gel, 2:1 petroleum ether/ethyl acetate) to give the corresponding amide (9.3 g, 73%) as a white crystal. Mp: 139−140.5 °C. ^{1}H NMR ($CDCl_3$): δ 7.30−7.20 (m, 15 H), 5.38 (br, 1 H), 4.13 (q, 2 H), 3.71 (d, 2 H), 3.64 (s, 2 H), 1.21 (t, 3 H). MS (EI): *m*/*z* 387 (M^+). Anal. Calcd for $C_{25}H_{25}O_3N$: C, 77.45; H, 6.46; N, 3.57. Found: C, 77.50; H, 6.50; N, 3.61. The compound (4.30 g, 11.1 mmol) was dissolved in 100 mL of hot ethanol, and 13 mL of 1 N aqueous NaOH solution was added. The solution was stirred at room temperature for 30 min. Then, most of the solvent was evaporated under reduce pressure. The solution was then acidified with 1 N HCl solution to pH = 2, and the resulting precipitate was collected, washed with CH_2Cl_2 (10 mL) and water completely, and then dried to give compound **5** (3.96 g, 99%) as a white solid. Mp: 220−222 °C. ^{1}H NMR ($CDCl_3$): δ 7.29−7.20 (m, 15 H), 5.35 (br, 1 H), 3.72 (s, 2 H), 3.65 (s, 2 H). MS (EI): *m*/*z* 359 (M^+). Anal. Calcd for $C_{23}H_{21}O_3N$·0.25H_2O: C, 76.16; H, 5.96; N, 3.49. Found: C, 75.90; H, 5.97; N, 3.85.

Compound 6. A suspension of DCC (1.80 g, 8.70 mmol), diamine **4** (0.83 g, 3.75 mmol), and compound **5** (2.70 g, 7.50 mmol) in THF (100 mL) was stirred at room temperature for 24 h. The mixture was filtered, and the filtrate was evaporated in vacuo to give a solid residue, which was purified by chromatography (silica gel, 20:1 dichloromethane/ethanol). Compound **6** (2.06 g, 59%) was obtained as a white power. Mp: 211−213 °C. ^{1}H NMR ($CDCl_3$): δ 7.27−7.17 (m, 30 H), 6.80 (s, 4 H), 6.04 (t, 2 H), 5.63 (t, 2 H), 3.87 (t, 4 H), 3.59 (s, 4 H), 3.52 (d, 4 H), 3.28 (m, 4 H), 1.85 (m, 4 H). MS (ESI): *m*/*z* 929 $(M + Na)^+$. Anal. Calcd for $C_{58}H_{58}O_6N_4$: C, 76.94; H, 6.45; N, 6.11. Found: C, 76.79; H, 6.46; N, 6.17.

***N*-(6-Bromohaxyl)phthalimide 8.** To a solution of 1,6-dibromohexane (18.5 mL, 0.12 mol) in DMF (50 mL) was added a solution of potassium phthalimide (7.40 g, 0.04 mol) in DMF (200 mL). The solution was then stirred at 90 °C for 24 h. After the mixture was cooled to room temperature, water (400 mL) was added and the mixture was extracted with chloroform (3 × 200 mL). The combined extracts were washed with 0.2 N NaOH solution (100 mL), water (2 × 100 mL), and brine (100 mL) and dried over anhydrous sodium sulfate. The solvent was then evaporated in vacuo, and the resulting residue was purified by chromatography (silica gel, 6:1 petroleum ether/ethyl acetate) to afford pure compound **8** (8.90 g, 72%) as white crystals. Mp: 56−57 °C. ^{1}H NMR ($CDCl_3$): δ 7.80 (m, 4 H), 3.79 (m, 2 H), 3.40 (m, 2 H), 2.10−2.30 (m, 8 H). MS (EI): *m*/*z* 309 (M^+), 311 $(M + 2)^+$. Anal. Calcd for $C_{14}H_{16}O_2NBr$: C, 54.03; H, 5.30; N, 4.51. Found: C, 54.20; H, 5.21; N, 4.51.

Compound 10a. This compound was prepared by using procedures similar to those described above for compound **4**. A suspension of 2 equiv of *N*-(3-bromopropyl)pathalimide **2** with diol **7**[5] in CH_3CN in the presence of excessive K_2CO_3 was refluxed for 48 h. After workup, the crude product **9a** was obtained. Compound **9a** was then treated with excessive hydrazine in refluxing ethanol. After workup, pure compound **10a** was obtained in 57% yield (for two steps) as a pale white solid. Mp: 98−99 °C. ^{1}H NMR (DMSO-d_6): δ 6.84 (s, 8 H), 3.99 (t, 4 H), 3.94 (t, 4 H), 3.70 (m, 8 H), 3.34 (br, 8 H), 1.77 (m, 4 H). MS (EI): *m*/*z* 492 (M^+). Anal. Calcd for $C_{26}H_{40}O_7N_2$: C, 63.47; H, 8.09; N, 6.00. Found: C, 63.38; H, 8.20; N, 5.68.

Compound 10b. This compound was prepared by using procedures similar to those described above for compound **4**. The reaction of diol **7** and bromide **8** in the presence of potassium carbonate in acetonitrile afforded compound **9b** (62%) as a white solid. Mp: 86−88 °C. ^{1}H NMR ($CDCl_3$): δ 7.83 (m, 4 H), 7.76 (m, 4 H), 6.84 (m, 8 H), 4.09 (t, 4 H), 3.92−

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3.83 (m, 8 H), 3.76−3.69 (m, 12 H), 1.79−1.71 (m, 8 H), 1.55−1.43 (m, 8 H). MS (EI): *m*/*z* 837 $(M + H)^+$. Anal. Calcd for $C_{48}H_{56}O_{11}N_2$: C, 68.55; H, 6.76; N, 3.02. Found: C, 68.87; H, 6.76; N, 3.35. Compound **9b** was then treated with hydrazine in hot ethanol to afford compound **10b** in 92% yield as a white solid after workup. Mp: 266−268 °C. ^{1}H NMR ($CDCl_3$): δ 7.02 (m, 8 H), 5.11 (s, 4 H), 4.22 (m, 4 H), 4.08 (t, 4 H), 3.99 (m, 4 H), 3.89 (m, 8 H), 3.11 (m, 4 H), 1.97−1.82 (m, 8 H), 1.71−1.62 (m, 8 H). MS (EI): *m*/*z* 576 (M^+). Anal. Calcd for $C_{32}H_{52}O_7N_2 \cdot H_2O$: C, 64.61; H, 9.17; N, 4.71. Found: C, 64.29; H, 9.27; N, 4.69.

Compound 11a. A suspension of DCC (1.80 g, 8.70 mmol), amino acid derivative **5** (2.70 g, 7.50 mmol), and diamine **10a** (1.80 g, 3.66 mmol) in THF (150 mL) was stirred at room temperature for 24 h. The solid was filtered off, and the filtrate was evaporated to give a solid residue. The residue was purified by chromatography (silica gel, 20:1 dichloromethane/ethanol) to give compound **11a** (2.58 g, 59%) as a white power. Mp: 89−90 °C. ^{1}H NMR ($CDCl_3$): δ 7.26−7.24 (m, 30 H), 6.83−6.75 (m, 8 H), 6.24 (br, 2 H), 5.86 (br, 2 H), 4.03 (t, 4 H), 3.82 (m, 8 H), 3.69 (m, 8 H), 3.57 (s, 4 H), 3.50 (s, 4 H), 3.24 (d, 4 H), 1.82 (m, 4 H). MS (ESI): *m*/*z* 1175 (M^+). Anal. Calcd for $C_{72}H_{78}O_{11}N_4$: C, 73.06; H, 6.83; N, 4.64. Found: C, 73.57; H, 6.69; N, 4.77.

Compound 11b. This compound was prepared in 51% yield as a white solid starting from compounds **5** and **10b** according to a procedure similar to that described above for compound **11a**. Mp: 84−85 °C. ^{1}H NMR ($CDCl_3$): δ 7.26−7.18 (m, 30 H), 6.84−6.76 (m, 8 H), 6.05 (br, 2 H), 5.89 (br, 2 H), 4.03 (t, 4 H), 3.83 (m, 8 H), 3.72 (m, 8 H), 3.60 (s, 4 H), 3.50 (d, 4 H), 3.05 (d, 4 H), 1.67 (m, 8 H), 1.32 (m, 8 H). MS (ESI): *m*/*z* 1259 (M^+). Anal. Calcd for $C_{78}H_{90}O_{11}N_4$: C, 74.36; H, 7.07; N, 4.35. Found: C, 74.37; H, 7.22; N, 4.45.

[2]Rotaxane 19a·4Cl. Compound **11a** (2.28 g, 1.94 mmol), dicationic compound **12**·2PF_6[5] (0.28 g, 0.40 mmol), and dibromide **13** (0.10 g, 0.40 mmol) were dissolved in CH_3CN (30 mL) and $CHCl_3$ (30 mL). The solution was stirred for 12 days at ambient temperature. After the solvent was removed under reduced pressure, the residue was subjected to column chromatography (silica gel), which was first treated with 10:1 $CHCl_3/C_2H_5OH$ as an eluent to elute the neutral compounds, with a 2 N aqueous solution of 7:1:2 $CH_3OH/CH_3NO_2/NH_4Cl$ as the eluent. The orange product fractions were combined, and the solvent was removed under reduced pressure. The residue was washed with cold water completely to give [2]rotaxane **19a**·4Cl (0.26 g, 36%) as a red solid. Mp: 166 °C dec. ^{1}H NMR (CD_3OD): δ 9.23 (d, 8 H), 8.17 (s, 8 H), 7.89 (s, 8 H), 7.28−7.14 (m, 30 H), 6.80−6.30 (br, 4 H), 5.98 (s, 8 H), 3.92−3.30 (m, 36 H), 1.90 (br, 4 H). MS (ESI): *m*/*z* 1802 $(M - Cl)^+$, 883 $(M - 2Cl)^{2+}$. Anal. Calcd for $C_{108}H_{110}O_{11}N_8Cl_4 \cdot 4H_2O$: C, 67.85; H, 6.41; N, 5.83. Found: C, 67.90; H, 6.24; N, 5.86.

[2]Rotaxane 14·4Cl. The compound was prepared as a red solid in 20% yield starting from compounds **6**, **12**·2PF_6, and **13** by using a procedure similar to that described in the preparation of **19a**·4Cl. Mp: 171 °C dec. ^{1}H NMR (CD_3OD): δ 9.29 (d, 8 H), 8.28 (d, 8 H), 7.91 (s, 8 H), 7.29−7.13 (m, 30 H), 5.73 (s, 8 H), 3.88 (s, 4 H), 3.67 (s, 4 H), 3.44 (br, 4 H), 3.31 (s, 4 H), 3.23 (br, 4 H), 2.02 (br, 4 H). MS (ESI): *m*/*z* 749 $(M - 2Cl)^{2+}$, 487 $(M - 3Cl)^{3+}$, 356 $(M - 4Cl)^{4+}$. Anal. Calcd for $C_{94}H_{90}O_6N_8Cl_4 \cdot 4H_2O$: C, 68.76; H, 6.03; N, 6.83. Found: C, 68.42; H, 6.14; N, 6.79.

[3]Rotaxane 18·4Cl. This [3]rotaxane was prepared in 31% yield as a red solid from the reaction of compounds **12**·2PF_6 and **13** in the presence of [2]rotaxane **17** by using a procedure similar to that described in the preparation of **19a**·4Cl. Mp: 172 °C dec. ^{1}H NMR (DMSO-d_6): δ 9.82 (br, 8 H), 9.49 (br, 4 H), 8.68 (br, 10 H), 8.00 (s, 2 H), 7.97 (s, 4 H), 7.94 (s, 8 H), 7.60 (br, 2 H), 7.35 (s, 8 H), 7.23−7.13 (m, 32 H), 5.86 (s, 8 H), 4.92 (br, 4 H), 4.23 (d, 4 H), 3.80 (s, 2 H), 3.67 (br, 4 H), 3.07−3.02 (m, 4 H), 2.73 (s, 4 H), 2.27 (s, 4 H), 1.89−1.78 (m, 4 H), 1.24 (s, 2 H). MS (ESI): *m*/*z* 490 $(M - 4Cl)^{4+}$. Anal. Calcd for $C_{126}H_{118}O_{10}N_{12}Cl_4 \cdot 4H_2O$: C, 69.59; H, 5.85; N, 7.73. Found: C, 69.25; H, 6.08; N, 7.69.

[2]Rotaxane 19b·4PF$_6$. This [2]rotaxane was prepared from the reaction of **11b**, **12**·2PF_6, and dibromide **13** in CH_3CN in 27% yield as a red solid following the procedure described for **19a**·4Cl after anion exchange with ammonium hexafluorophosphate. Mp: 166 °C dec. ^{1}H NMR (DMSO-d_6): δ 9.49 (d, 8 H), 8.41 (d, 8 H), 7.99 (s, 8 H), 8.05 (br, 2 H), 7.57 (br, 2 H), 7.24−7.17 (m, 30 H), 5.91 (s, 8 H), 3.81−3.35 (m, 36 H), 3.08 (br, 4 H), 1.74 (br, 4 H), 1.44 (br, 12 H). MS (ESI): *m*/*z* 1035.5 $(M - 2PF_6)^{2+}$, 642 $(M - 3PF_6)^{3+}$, 445 $(M - 4PF_6)^{4+}$. Anal. Calcd for $C_{114}H_{122}O_{11}N_8P_4F_{24} \cdot 4H_2O$: C, 56.27; H, 5.52; N, 4.52. Found: C, 56.28; H, 5.40; N, 4.60.

[2]Rotaxane 20a. A solution of isophthaloyl dichloride **15** (2.03 g, 10.0 mmol) in anhydrous chloroform (50 mL) and a solution of *p*-xylylenediamine **16** (1.36 g, 10.0 mml) in anhydrous chloroform (50 mL) were added simultaneously over a period of 5 h at room temperature with stirring to a solution of compound **11a** (1.20 g, 1.02 mmol) and triethylamine (2.76 mL, 20.0 mmol) in anhydrous chloroform (50 mL). The mixture was then stirred at room temperature for another 12 h. The solid was filtered off. The filtrate was washed with 1 N HCl solution (3 × 100 mL), 5% $NaHCO_3$ solution (3 × 100 mL), water (100 mL), and brine (100 mL) and then dried over anhydrous sodium sulfate. The solvent was evaporated in vacuo, and the resulting residue was purified by chromatography (silica gel, 20:1 $CHCl_3$/CHOH) to give [2]rotaxane **20a** (0.31 g, 18%) as a white solid. Mp: 108−110 °C. ^{1}H NMR ($CDCl_3$): δ 8.19 (s, 2 H), 8.12 (d, 4 H), 7.56 (m, 2 H), 7.45 (s, 4 H), 7.28−7.13 (m, 30 H), 7.00 (s, 8 H), 6.71−6.62 (m, 8 H), 6.50 (br, 2 H), 5.70 (br, 2 H), 4.43 (s, 8 H), 3.93 (s, 4 H), 3.71 (m, 8 H), 3.57 (m, 8 H), 3.53 (s, 4 H), 2.98 (m, 8 H), 1.68 (m, 4 H). MS (ESI): *m*/*z* 1709 (M^+). Anal. Calcd for $C_{104}H_{106}O_{15}N_8 \cdot H_2O$: C, 72.30; H, 6.26; N, 6.02. Found: C, 72.36; H, 6.32; N, 6.49.

[2]Rotaxane 17. The compound was prepared in 19% yield as a white solid from the reaction of compounds **6**, **15**, and **16** in chloroform by using a procedure similar to that described in the preparation of rotaxane **20a**. Mp: 197−198 °C. ^{1}H NMR (1:2 $CD_3OD/CDCl_3$): δ 8.19 (s, 2 H), 8.08 (d, 4 H), 7.58 (t, 2 H), 7.48 (s, 4 H), 7.26−7.13 (m, 30 H), 7.07 (s, 8 H), 6.62 (s, 4 H), 4.42 (s, 8 H), 3.68 (t, 4 H), 3.48 (s, 4 H), 3.02 (s, 4 H), 2.90−2.99 (m, 4 H), 1.67 (m, 4 H). MS (ESI): *m*/*z* 1463 $(M + Na)^+$. Anal. Calcd for $C_{90}H_{86}O_{10}N_8 \cdot 2H_2O$: C, 73.56; H, 6.18; N, 7.59. Found: C, 73.24; H, 6.16; N, 7.59.

[2]Rotaxane 20b. The rotaxane was prepared in 18% yield as a white solid from the reaction of **11b**, **15**, and **16** in chloroform by using a procedure similar to that described in the preparation of rotaxane **20a**. Mp: 94−95 °C. ^{1}H NMR ($CDCl_3$): δ 8.18 (s, 2 H), 8.09 (d, 4 H), 7.53 (m, 6 H), 7.28−7.13 (m, 30 H), 7.05 (s, 8 H), 6.74 (s, 8 H), 6.50 (br, 1 H), 5.70 (br, 1 H), 4.45 (s, 8 H), 3.96 (t, 4 H), 3.79 (t, 4 H), 3.73 (s, 4 H), 3.58 (s, 4 H), 3.02 (br, 3 H), 2.77 (br, 3 H), 2.00 (br, 2 H), 1.63 (m, 4 H), 1.25 (m, 10 H), 1.11 (m, 4 H). MS (ESI): *m*/*z* 1793 $(M + H)^+$. Anal. Calcd for $C_{110}H_{118}O_{15}N_8$: C, 73.53; H, 6.81; N, 5.95. Found: C, 73.71; H, 6.65; N, 6.24.

[3]Rotaxane 21a·4Cl. This [3]rotaxane was prepared in 54% yield as a red solid from the reaction of compounds **12**·2PF_6 and **13** in the presence of [2]rotaxane **20a** by using a procedure similar to that described in the preparation of **19a**·4Cl. Mp: 110 °C dec. ^{1}H NMR (DMSO-d_6): δ 9.90 (br, 4 H), 9.78 (br, 4 H), 9.49 (br, 4 H), 8.78 (br, 4 H), 8.67 (br, 4 H), 8.20 (s, 2 H), 8.14 (d, 4 H), 7.99 (s, 8 H), 7.67 (t, 2 H), 7.31 (s, 8 H), 7.19 (s, 32 H), 6.60 (br, 2 H), 5.92 (br, 8 H), 4.95 (d, 4 H), 4.26 (d, 4 H), 3.93−2.72 (m, 40 H), 1.96 (br, 2 H), 1.68 (br, 2 H). MS (ESI): *m*/*z* 1149 $(M - 2Cl)^{2+}$, 754 $(M - 3Cl)^{3+}$, 557 $(M - 4Cl)^{4+}$. Anal. Calcd for $C_{140}H_{138}O_{15}N_{12}Cl_4 \cdot 4H_2O$: C, 68.83; H, 6.04; N, 6.88. Found: C, 68.47; H, 6.20; N, 6.84.

[3]Rotaxane 21b·4Cl. This [3]rotaxane was prepared in 47% yield as a red solid from the reaction of compounds **12**·2PF_6 and **13** in the presence of [2]rotaxane **20b** by following the procedure described for preparing **19a**·4Cl. Mp: 168 °C dec. ^{1}H NMR (CD_3OD): δ 9.94 (br, 4 H), 9.31 (br, 4 H), 8.87 (br, 4 H), 8.24 (br, 4 H), 8.18 (s, 2 H), 7.99 (s, 12 H), 7.59 (t, 2 H), 7.34 (s, 8 H), 7.20 (m, 30 H), 6.30 (d, 2 H), 6.15 (d, 2 H), 6.03 (d, 4 H), 5.89 (d, 4 H), 4.96 (d, 4 H), 4.30 (d, 4 H), 3.99 (m, 8 H), 3.81−3.35 (m, 20 H), 3.10 (m, 4 H), 2.61 (br, 2 H), 2.39 (m, 2 H), 1.36 (m, 2 H), 1.13−1.08 (m, 8 H), 0.50 (m, 2 H),

0.06 (br, 2 H), −0.31 (br, 2 H). MS (ESI): *m*/*z* 783 $(M - 3Cl)^{3+}$, 578 $(M - 4Cl)^{4+}$. Anal. Calcd for $C_{146}H_{150}O_{15}N_{12}Cl_4 \cdot 4H_2O$: C, 69.39; H, 6.32; N, 6.65. Found: C, 69.02; H, 6.40; N, 6.62.

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