JOC Article

Self-Assembly of Novel [3]- and [2]Rotaxanes Based on Donor−Acceptor and Hydrogen-Bonding Interactions. Intensified Inter-Ring Repulsion Interaction and Shuttling Behavior

Lin Chen,[†] Xin Zhao,[‡] Yan Chen,[†] Cheng-Xue Zhao,[†] Xi-Kui Jiang,[‡] and Zhan-Ting Li*[,‡]

School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, 800 Dongchuan Lu, Shanghai 200240, China, and Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

ztli@pub.sioc.ac.cn.

Received August 30, 2002

Three novel hetero[3]rotaxanes, which comprise one neutral tetraamide cyclophane, one tetracationic cyclophane, and one linear component, have been assembled by utilizing hydrogen-bonding and donor−acceptor interactions, through three neutral [2]rotaxanes as intermediates. Three tetracationic [2]rotaxanes are also prepared for property comparison. For all three linear components, diamide subunits, the hydrogen-bonding templating moieties, are introduced at the center of the molecules, while the electron-rich hydrogquinone subunits, the donor−acceptor interaction templates, are incorporated between the diamides and the triphenylmethyl stoppers. Compared with the reported [3]rotaxanes, the novel hetero[3]rotaxanes exhibit remarkably intensified spatial interaction between the two ring components, which had been proved by ^{1}H NMR and UV study. For the first time, inter-ring NOEs are observed for interlocked [3]rotaxanes.

Introduction

Rotaxanes are one class of supramolecular structures that have been investigated vigorously in the past decade.[1] These supramolecules not only have exhibited great potential for applications in smart molecular devices and materials science but also are optimal supramolecular platforms for investigating novel rules of noncovalent interactions.[2] With the progress of synthetic supramolecular chemistry, several general and efficient methods have been developed, and consequently a large number of [2]rotaxanes and [3]rotaxanes have been self-assembled.[3] Many of the [2]rotaxanes display the unique shuttling movement of the cyclic components along the linear component, which might be controlled by chemical,[4] electrochemical[5] or optical exciting[6] methods. However, these studies have always focused on the interactions between the linear component and the cyclic component(s). Probably as a result of the lack of suitable model structures, to our knowledge, investigations on the

[†] Shanghai Jiaotong University.

[‡] Shanghai Institute of Organic Chemistry.

(1) (a) Hoss, R.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 375. (b) Johnston, A. G.; Leigh, D. A.; Pritchard, R. J.; Deegan, M. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1209. (c) Gibson, H. W. In *Large Ring Molecules*; Semlyen, J. A., Eds.; John Wiley & Sons: New York, 1996; pp 191−262. (d) Philp, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1155. (e) *Catenanes, Rotaxanes and Knots*; Sauvage, J.-P., Dietrich-Buchecker, C. O., Eds.; Wiley-VCH: Weinheim, 1999. (f) Lindoy, L. F.; Atkinson, I. M. *Self-Asembly in Supramolecular Systems*; Royal Society of Chemistry: Cambridge, 2000. (g) Breault, G. A.; Hunter, C. A.; Mayers, P. C. *Tetrahedron* **1999**, *55*, 5265. (h) Raymo, F. M.; Stoddart, J. F. *Chem. Rev.* **1999**, *99*, 1643. (i) Hubin, T. J.; Busch, D. H. *Coord. Chem. Rev.* **2000**, *200*, 5. (j) Reuter, C.; Schmieder, R.; Vögtle, F. *Pure Appl. Chem.* **2000**, *72*, 2233. (k) Cantrill, S. J.; Pease, A. R.; Stoddart, J. F. *J. Chem. Soc., Dalton Trans.* **2000**, 3715. (l) Mahan, E.; Gibson, H. W. In *Cyclic Polymers*; Semlyen, J. A., Ed.; Kluwer Publishers: Dordrecht, 2000; pp 415−560. (m) Raehm, L.; Sauvage, J.-P. *Struct. Bonding* **2001**, *99*, 55.

(2) (a) Balzani, V.; Gómez-López, M.; Stoddart, J. F. *Acc. Chem. Res.* **1998**, *31*, 405. (b) Kaifer, A. E. *Acc. Chem. Res.* **1999**, *32*, 62. (c) Collier, C. P.; Wong, E. W.; Belohradský, M.; Raymo, F. M.; Stoddart, J. F.; Kuekes, P. J.; Williams, R. S.; Heath, J. R. *Science* **1999**, *285*, 391. (d) Brouwer, A. M.; Frochot, C.; Gatti, F. G.; Leigh, D. A.; Mottier, L.; Paolucci, F.; Roffia, S.; Wurpel, G. W. H. *Science* **2001**, *291*, 2124.

(3) For some recent examples, see: (a) Asakawa, M.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Belohradsky, M.; Gandolfi, M. T.; Kocian, O.; Prodi, L.; Raymo, F. M.; Stoddart, J. F.; Venturi, M. *J. Am. Chem. Soc.* **1997**, *119*, 302. (b) Gong, C.; Gibson, H. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 310. (c) Clegg, W.; Gimenez-Saiz, C.; Leigh, D. A.; Mruphy, A.; Slawin, A. M. Z.; Teat, S. J. *J. Am. Chem. Soc.* **1999**, *121*, 4124. (d) Easton, C. J.; Lincoln, S. F.; Meyer, A. G.; Onagi, H. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2501. (e) Fabicon, R. M.; Parvez, M.; Richey, H. G., Jr. *Organometallics* **1999**, *18*, 5163. (f) Baer, A. J.; Macartney, D. H. *Inorg. Chem.* **2000**, *39*, 1410. (g) Chichak, K.; Walsh, M. C.; Branda, N. R. *Chem. Commun.* **2000**, 847. (h) Buston, J. E. H.; Young, J. R.; Anderson, H. L. *Chem. Commun.* **2000**, 905. (i) Loeb. S. J.; Wisner, J. A. *Chem. Commun.* **2000**, 1939. (j) Jeppesen, J. O.; Perkins, J.; Becher, J.; Stoddart, J. F. *Org. Lett.* **2000**, *2*, 3547. (k) Shukla, R.; Deetz, M. J.; Smith, B. D. *Chem. Commun.* **2000**, 2397. (l) Linke, M.; Chambron, J.-C.; Heitz, V.; Sauvage, J.-P.; Encinas, S.; Barigelletti, F.; Flamigni, L. *J. Am. Chem. Soc.* **2000**, *122*, 11834.

(4) (a) Bissell, R. A.; Córdova, E.; Kaifer, A. E.; Stoddart, J. F. *Nature* **1994**, *369*, 133. (b) Martínez-Díaz, M.-V.; Spencer, N.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1904. (c) 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.

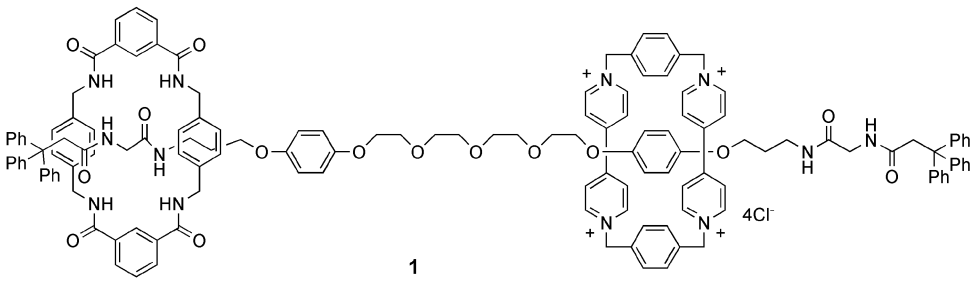
(5) (a) Armaroli, N.; Balzani, V.; Collin, J.-P.; Gaviña, P.; Sauvage, J.-P.; Ventura, B. *J. Am. Chem. Soc.* **1999**, *121*, 4397. (b) Collin, J.-P.; Dietrich-Buchecker, C.; Gaviña, P.; Jimenez-Molero, M. C.; Sauvage, J.-P. *Acc. Chem. Res.* **2001**, *34*, 477.

(6) (a) Ashton, P. R.; Ballardini, R.; Balzani, V.; Credi, A.; Dress, K. R.; Ishow, E.; Kleverlaan, C. J.; Kocian, O.; Preece, J. A.; Spencer, N.; Stoddart, J. F.; Venturi, M.; Wenger, S. *Chem. Eur. J.* **2000**, *6*, 3558. (b) Wurpel, G. W. H.; Brouwer, A. M.; van Stokkum, I. H. M.; Farran, A.; Leigh, D. A. *J. Am. Chem. Soc.* **2001**, *123*, 11327. (c) Brouwer, A. M.; Frochot, C.; Gatti, F. G.; Leigh, D. A.; Mottier, L.; Paolucci, F.; Roffia, S.; Wurpel, G. W. *Science* **2001**, *291*, 2124.

10.1021/jo026370i CCC: $25.00

Published on Web 02/21/2003

CHART 1



1

inter-ring interactions of more complex [3]rotaxanes have never been reported, although such investigations are potentially useful for exploring new principles to control the relative orientation of components within supramolecules and for further developing new generation of supramolecular systems.

We recently reported a general approach to assembling hetero[3]rotaxane (**1**), which consists of a dipyridinium tetracationic cyclophane, a neutral tetraamide cyclophane, and a linear template, by combining the well-established donor−acceptor interaction and intermolecular hydrogen-bonding principles.[7] This novel type of hetero[3]rotaxanes not only represents a new class of rotaxane hybrids but also exhibits novel unique dynamic properties, which are not available in homo[3]rotaxanes. For example, the activation energy for the shuttling of the tetracationic cyclophane along the linear component was substantially lowered as a result of the presence of the neutral cyclophane. Moreover, the autorotation of the dipyridinium within the tetracationic cyclophane was also revealed because of the asymmetry of the [3]-rotaxanes. However, direct evidence could not be observed for the possible spatial interaction between the two different ring components. To more systematically study this possible inter-ring interaction and also to investigate the scope and limitation of the self-assembly of this novel kind of [3]rotaxanes, we had designed a new series of linear molecules, in which the hydrogen-bonding templating subunits are incorporated between two hydroquinone subunits at the center of the molecules. We herein report the self-assembly of nine new hetero[3]-rotaxanes and [2]rotaxanes from these linear templating molecules and a detailed investigation of their dynamic behavior.

Results and Discussion

Synthesis and Self-Assembly. Three linear templates, **10**, **14a**, and **14b**, were designed and synthesized. Different from the previously reported templates, in which the glycine moieties are directly connected to the stoppers,[7] all three compounds **10**, **14a**, and **14b** are incorporated with two unnatural amide moieties as hydrogen-bonding assembling templates at the center of the molecules. In addition, the two amide moieties are connected by very short aliphatic linkers, to facilitate their ability to cooperatively template the formation of the neutral tetraamide cyclophane,[8] and two hydroquinone subunits, to induce the generation of the tetracationic macrocycle,[9] are incorporated between the amides and the stoppers. It is expected that, within the new hetero[3]rotaxnes assembled based on them, the intermolecular hydrogen bonding between the neutral macrocycle and the *central* amides of the linear compounds, if any, would impose greater spatial repulsion on the tetracationic cyclophane and consequently affect the shuttling behavior of the tetracationic cyclophane along the linear components, as shown in Figure 1.

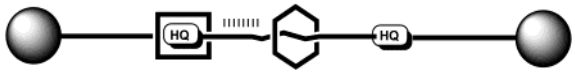


FIGURE 1. Cartoon showing the inter-ring interactions within the new hetero[3]rotaxanes. The neutral and tetracationic cyclophanes are represented by the hexagon and tetragon, respectively.

Compound **10** was synthesized as described in Scheme 1. Compound **2** reacted with an excess of dibromide **3** in refluxed acetonitrile in the presence of potassium carbonate to afford bromide **4** in good yield, which further coupled with phenol **5** to afford compound **6**. Compound **6** was then hydrogenated in ethanol in the presence of Pd−C to produce phenol **7** in quantitative yield. Compound **7** was further converted to **8**, which was hydrolyzed to afford **9**. Compound **9** was then treated with ethylenediamine in the presence of DCC and HOBt in ethyl acetate to generate the first template, **10**.

The synthesis of template compounds **14a** and **14b** is shown in Scheme 2. Compound **4** was first alkylated with bromide **11** to give compound **12**, which was hydrolyzed with hydrazine to produce amine **13**. Treatment of compound **13** with malonic acid or succinic acid in the presence of DCC afforded compounds **14a** and **14b**, respectively. For all three molecules **10**, **14a**, and **14b**, the triphenylmethylphenol group was chosen as the stopper for its synthetic convenience.

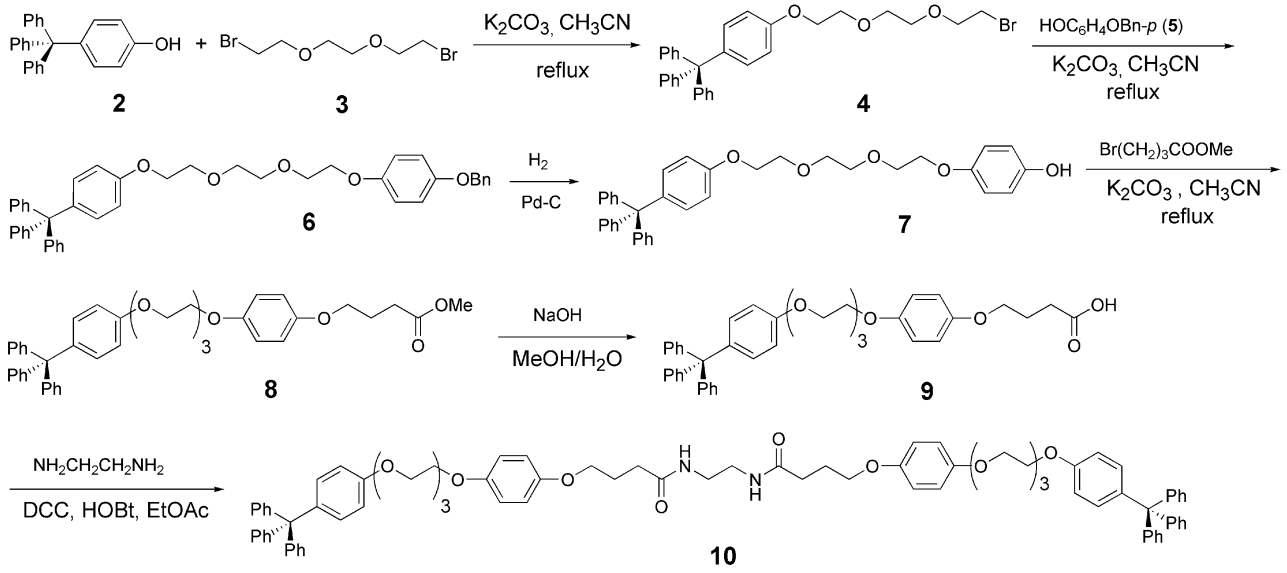
Two [2]rotaxanes and one [3]rotaxane were then assembled from the template molecule **10**, as shown in Scheme 3. Thus, treatment of compound **10** with dicationic salt **15**·2PF_6 and dibromide **16** in DMF at room temperature for 10 days afforded tetracationic [2]rotaxane **17**·4Cl in 34% yield after column chromatography, whereas the reaction of 1,3-phthaloyl dichloride **18** and diamine **19** in chloroform in the presence of **10** at room

(7) Zhao, X.; Jiang, X.-K., Shi, S.; Yu, Y.-H.; Xia, W.; Li, Z.-T. *J. Org. Chem.* **2001**, *66*, 7035.

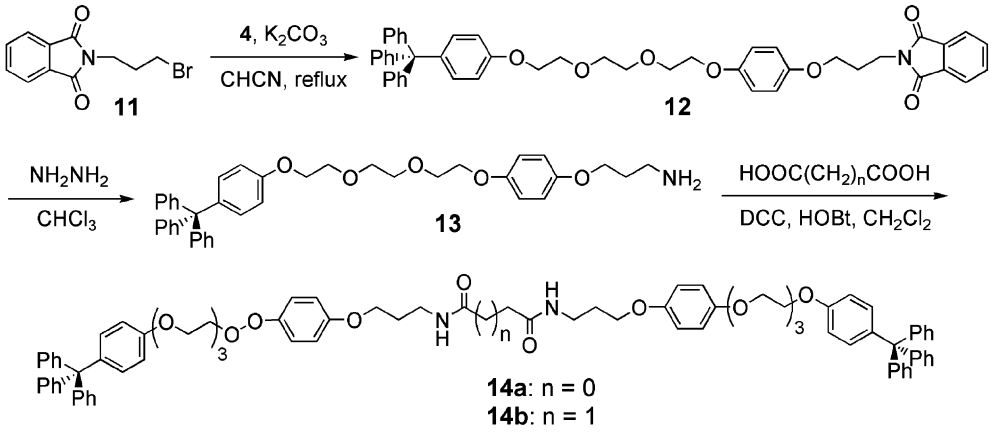
(8) Johnston, A. G.; Leigh, D. A.; Nezhat, L.; Smart, J. P.; Deegan, M. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1212.

(9) Anelli, P. L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, M. T.; Goodnow, 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.

SCHEME 1



SCHEME 2



temperature led to the formation of neutral [2]rotaxane **20** in 24% yield. In the presence of [2]rotaxane **20**, the reaction of **15**·2PF_6 with **16** in DMF at room temperature for 10 days gave the hetero[3]rotaxane **21**·4Cl in 31% yield.

With compounds **14a** and **14b** as templates, the reactions of dication **15**·2PF_6 with dibromide **16** in DMF gave another two ionic [2]rotaxanes **22a**·4Cl and **22b**·4Cl, and the reactions of compound **18** with diamine **19** afforded neutral [2]rotaxanes **23a** and **23b**, respectively. These two neutral [2]rotaxanes were further utilized as templates to assemble tetracationic [3]rotaxanes **24a**·4Cl and **24b**·4Cl after column chromatography, as shown in Scheme 4.

For all reactions to assemble [3]rotaxanes, no [4]-rotaxanes with two tetracationic rings were detected. It was reported that the ability of amide derivatives to template the formation of [2]rotaxanes varies greatly depending on their structures.[8,10] The present three linear compounds **10** and **14a**,**b** exhibit comparable templating ability, although the incorporated amide subunits are quite different. As had been observed in a previous report,[7] the assembly yields of all of the hetero[3]-rotaxanes are higher than those for the neutral [2]-rotaxanes.

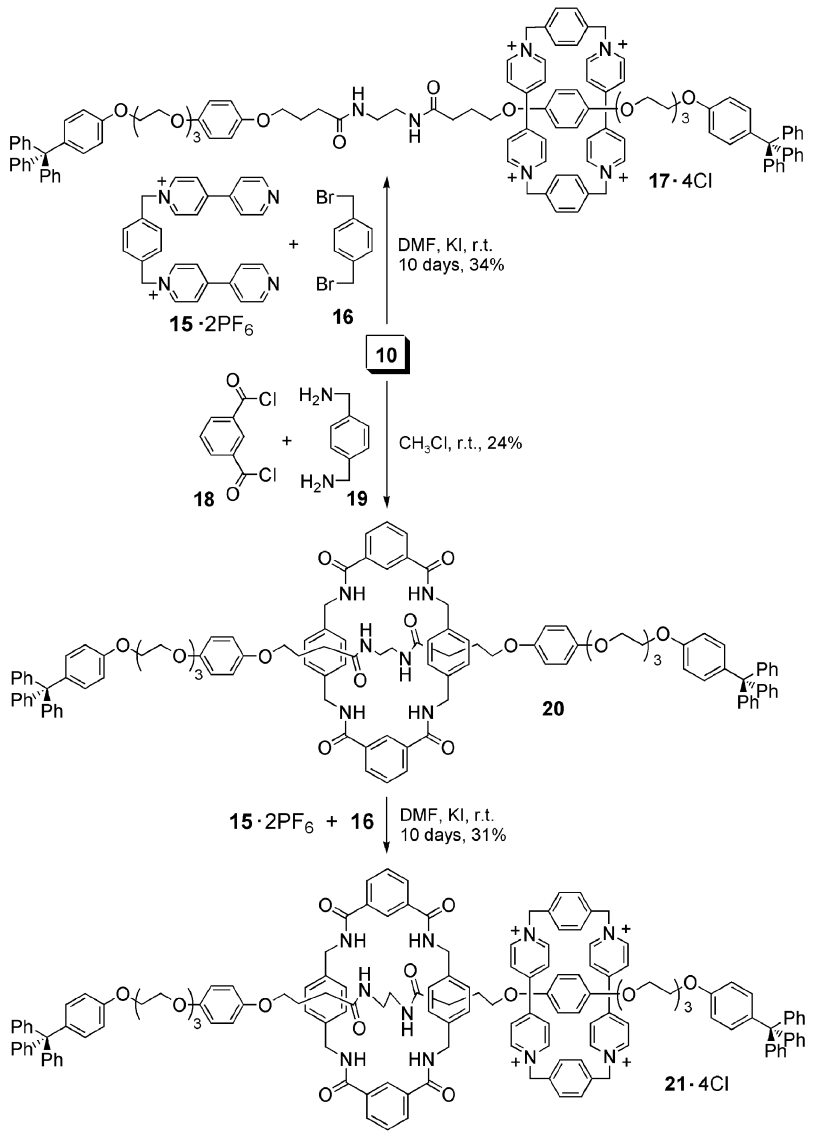
^{1}H NMR Spectroscopy and Shuttling Properties. The structures of the [2]- and [3]rotaxanes have been characterized by ^{1}H NMR and MS spectra and elemental analysis. Significant upfield shifts were observed for aliphatic protons of the linear part of all rotaxanes as a result of the shielding of the ring components. The shuttling properties of the three tetracationic [2]rotaxanes were first investigated by variable temperature ^{1}H NMR, and the activation energies for the shuttling processes of the ionic cyclophane between the hydroquinone stations, obtained with the coalescence method,[11] are listed in Table 1. It can be seen that the values for these new [2]rotaxanes are comparable to those of the previously reported [2]rotaxanes,[7,12] in which two hydroquinone subunits are connected with a tetra(ethyleneoxyl) chain in the linear components. The results reveal that in

(10) Gatti, F. G.; Leigh, D. A.; Nepogodiev, S. A.; Slawin, A. M. Z.; Teat, S. J.; Wong, J. K. Y. *J. Am. Chem. Soc.* **2001**, *123*, 5983.

(11) Sandstroom, J. In *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; Chapter 6.

(12) Anelli, P.-L.; Asakawa, M.; Ashton, P. R.; Bissell, R. A.; Clavier, G.; Górski, R.; Kaifer, A. E.; Langford, S. J.; Mattersteig, G.; Menzer, S.; Philp, D.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Williams, D. J. *Chem. Eur. J.* **1997**, *3*, 1113.

SCHEME 3



highly polar solvents, there are no substantial interaction between the tetracationic cyclophane and the centrally located amide moieties of the linear components.

Within the temperature range from 210 to 298 K, no shuttling behavior was observed for neutral [2]rotaxanes **20**, **23a**, and **23b** in chloroform-*d*. This may be attributed to the fact that the two amides in all three linear components are very close and the macrocyclic component may be positioned in a conformation such as to be able to form hydrogen bonds with both amides of the linear molecules simultaneously, which means that there is actually no shuttling behavior of the cyclophane between the two amide stations.[13] Since no further splitting was observed for all the proton signals of the cyclophane in [2]rotaxanes **20**, **23a**, and **23b** within the above temperature range, the two chairlike conformations observed in the solid-state structures of several related [2]rotaxanes should, if any, undergo fast exchange on the ^{1}H NMR time scale.[10] 2D-NOESY and COSY spectra did not show NOEs between the ring and linear components for the three neutral [2]rotaxanes. This observation is quite different from that reported by Leigh[13] and may be attributed to the existence of many ethyleneoxyl groups in the linear components. These ethylene-linked oxygens may compete with the CO oxygens in the linear components to bind the NH protons in the ring component by hydrogen bonding, making it impossible for selective positioning of the ring component around the central amide subunits.

[3]Rotaxanes **21**·4Cl, **24a**·4Cl, and **24b**·4Cl are asymmetric because they comprise two different rings and therefore display much more complicated ^{1}H NMR spectra. The ^{1}H NMR signals of these [3]rotaxanes have been assigned on the basis of 2D-NOESY and COSY techniques. The methylene protons of the neutral rings of all three [3]rotaxanes exhibit two sets of doublets. However, the xylene protons give only one singlet even at the low temperature of 210 K, showing that the benzenes always rotate quickly around the methylenes-built axis on the ^{1}H NMR time scale. Generally, NOEs were observed between both α- and *β*-protons of the cyclophane pyri-

(13) (a) Lane, A. S.; Leigh, D. A.; Murphy, A. *J. Am. Chem. Soc.* **1997**, *119*, 11092. (b) Leigh, D. A.; Murphy, A.; Smart, J. P.; Slawin, A. M. Z. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 728.

SCHEME 4

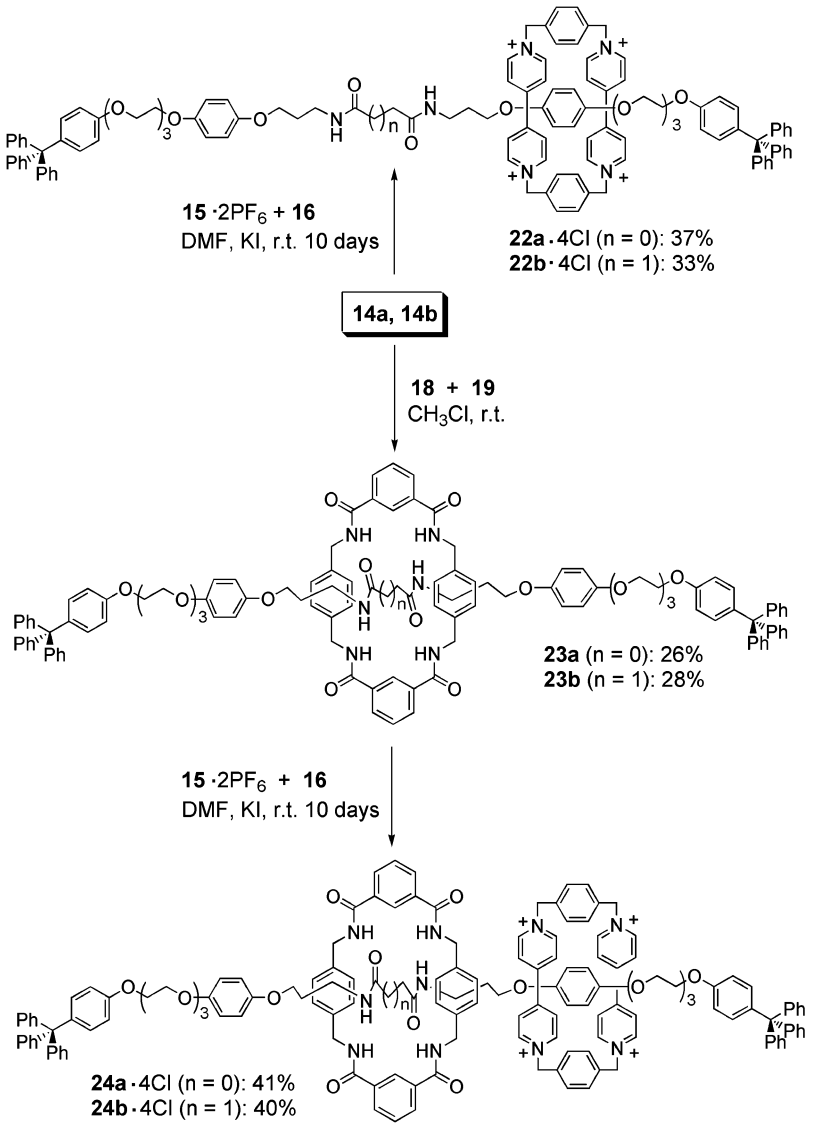


TABLE 1. Kinetic and Thermodynamic Parameters of Ionic [2]Rotaxanes in Methanol-*d* Based on the Temperature-Dependent ^{1}H NMR Method

rotaxanes	probe	$\Delta\nu$ (Hz)[a]	k_c (s^{-1})	T_c (K)[b]	$\Delta G^{\ddagger}$ (kcal^{-1} mol^{-1})
17·4Cl	α-CH[c]	51 ± 4	113 ± 9	268	13.1 ± 0.2
17·4Cl	*β*-CH[d]	58 ± 4	129 ± 9	268	13.1 ± 0.2
22a·4Cl	α-CH	53 ± 5	117 ± 11	268	13.1 ± 0.2
22b·4Cl	α-CH[c]	56 ± 4	124 ± 9	268	13.1 ± 0.2
22b·4Cl	*β*-CH[d]	40 ± 4	189 ± 9	263	12.9 ± 0.2

[a] The errors represent the deviations from the average values of three experiments. [b] With an error of ±5 °C. [c] CH α to the pyridine N of the tetracationic ring. [d] CH *β* to the pyridine N of the tetracationic ring.

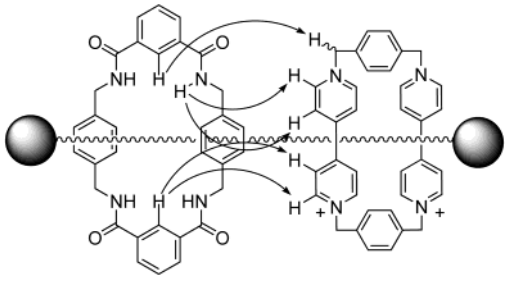


FIGURE 2. NOEs observed between the protons of the two ring components of [3]rotaxanes **21**·4Cl. The linear component is represented by cartoon for clarity.

diniums and many ethyleneoxy protons of the linear components in methanol-*d*. A number of NOEs were also detected between the neutral and ionic ring components, and the results obtained for [3]rotaxanes **21**·4Cl is presented in Figure 2 as an example. This observation provides direct evidence to support that there are significant spatial repulsion between the two ring components. To our knowledge, this is the first observation of inter-ring NOEs for [3]rotaxanes. In principle, spatial repulsion always exists between ring components of [3]rotaxanes. However, such spatial interaction could not be measured by the NOE technique for homo[3]-rotaxanes, since it is impossible to determine if such possible NOEs come from intra-ring or inter-ring interactions for homo[3]rotaxanes. It is noteworthy that no similar NOEs had ever detected for previously reported hetero[3]rotaxanes.[7] Therefore, this observation indicates that inter-ring interaction could be improved by simple

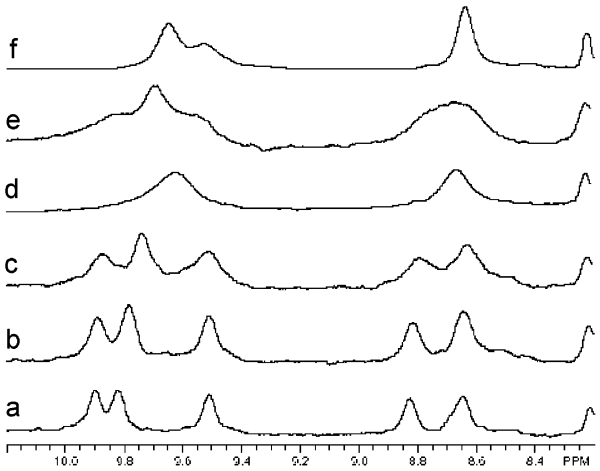


FIGURE 3. Partial variable temperature ^{1}H NMR spectra (400 HMz, DMSO-d_6) of **24b**·4Cl at (a) 293, (b) 303, (c) 313, (d) 323, (e) 333 K, and (f) 343 K, showing that the separated signals gradually combine to afford a new singlet for both α- and β-pyridinium protons.

TABLE 2. Kinetic and Thermodynamic Parameters for Rotation of Dipyridinium Units around the Methylenes-Built Axis in [3]Rotaxanes in DMSO-d_6, Based on ^{1}H NMR Spectra

rotaxane	probe[a]	$\Delta\nu$ (Hz)[b]	k_c (s^{-1})	T_c (K)[c]	$\Delta G^{\ddagger}$ ($kcal^{-1}\ mol^{-1}$)
21·4Cl	α-CH	117 ± 10	259 ± 22	335	16.0 ± 0.3
21·4Cl	β-CH	132 ± 6	293 ± 13	340	16.2 ± 0.2
24a·4Cl	α-CH	136 ± 8	301 ± 18	333	15.8 ± 0.2
24a·4Cl	β-CH	82 ± 8	182 ± 18	325	15.7 ± 0.2
24b·4Cl	α-CH	156 ± 5	346 ± 11	333	15.8 ± 0.1
24b·4Cl	β-CH	72 ± 5	160 ± 11	328	16.0 ± 0.1

[a] The pyridine CHs of the tetracationic ring. [b] The errors represent the deviations from the average values of three experiments. [c] With an error of ±5 °C.

re-location of the templating moieties of the linear components.

At room temperature, both the α- and β-protons of the dipyridiniums of the tetracationic cyclophane of all [3]-rotaxanes **21**·4Cl, **24a**·4Cl, and **24b**·4Cl in DMSO-d_6 display two separated signals, indicating that the rotation of the dipyridinium subunits around the axis of the two linked methylene groups are slow on the ^{1}H NMR time scale.[7] With the increase of the temperature, both α- and β-proton signals gradually combine and generate a new broad signal, respectively, as shown in Figure 3 for **24b**·4Cl. The values of the activation energy $\Delta G^{\ddagger}$ for this rotating processed are obtained by using the coalescence method and are presented in Table 2.[14]

Variable temperature ^{1}H NMR study reveals that hetero[3]rotaxanes **21**·4Cl, **24a**·4Cl, and **24b**·4Cl also display significant temperature dependence at reduced temperature. For example, both the α- and β-pyridinium protons of **24b**·4Cl exhibit a broad signal, respectively, in methanol-*d* at room temperature, indicating that both the rotation of the pyridiniums described above and the shuttling process of the ionic cyclophane are fast on the NMR time scale. With the lowering of the temperature, these signals gradually split into two and then four separated signals. This observation may be rationalized by considering that the corresponding rotation and shuttling processes mentioned above are lowered and finally stopped on the NMR time scale at reduced temperature. On the basis of the previously reported work,[7] the second splitting process was ascribed as the result of the shuttling process of the tetracationic cyclophane. The free energies of activation associated with this shuttling process of the [3]rotaxanes can be derived with the coalescence method and are presented in Table 3.[15] Considering the error of the coalescence method, the values are actually comparable, showing that the change of the center-positioned amides have no substantial effect on the shuttling process. The results also support the opinion that, as had been observed in several related hetero[3]rotaxanes,[7] the neutral cyclophane in these new hetero[3]rotaxanes also always imposed repelling on the tetracationic cyclophane and remarkably affected the later's shuttling behavior as shown in Figure 1.

TABLE 3. Data Associated with [3]Rotaxanes Associated with Shuttling Behavior of Tetracationic Cyclophane in [3]Rotaxanes in Methanol-*d*, Based on the ^{1}H NMR Method

rotaxanes	probe[a]	$\Delta\nu$ (Hz)[b]	k_c (s^{-1})	T_c (K)[c]	$\Delta G^{\ddagger}$ ($kcal^{-1}\ mol^{-1}$)
21·4Cl	α-CH	216 ± 10	477 ± 22	288	13.3 ± 0.1
21·4Cl	β-CH	204 ± 12	452 ± 26	275	12.7 ± 0.1
24a·4Cl	α-CH	251 ± 12	556 ± 26	283	13.0 ± 0.1
24a·4Cl	β-CH	250 ± 15	553 ± 30	288	13.2 ± 0.2
24b·4Cl	α-CH	229 ± 20	506 ± 44	278	12.8 ± 0.2
24b·4Cl	β-CH	258 ± 14	571 ± 31	283	12.9 ± 0.1

[a] The pyridine CHs of the tetracationic ring. [b] The errors represent the deviations from the average values of three experiments. [c] With an error of ±5 °C.

Electronic Absorption Spectra. The UV−vis properties of all of the linear compounds, [2]- and [3]rotaxanes, were investigated in methanol. A summary of the absorption data is presented in Table 4. The absorption bands observed for **10**, **14a**, and **14b**, all with maxima at 286 nm, are ascribed to the hydroquinone units. Similar absorption bands are also observed for the neutral [2]rotaxanes **20**, **23a**, and **23b** with the same absorption maxima, indicating that the neutral cyclophane in these [2]rotaxanes have no significant influence on the electronic property of the hydroquinone units. As expected, intense charge-transfer absorption bands were observed for all the ionic [2]- and [3]rotaxanes, as s result of the donor−acceptor interaction between the bipyridinium and hydroquinone units.[7,9]

It is found that the values of the [3]rotaxanes are obviously reduced compared with those of reported [3]-rotaxanes (**1**),[7] in which the amide subunits are incorporated between the center-positioned hydroquinone

(14) A series of [2]rotaxanes had been reported in which the dipyridinium units rotate around their nitrogen−nitrogen axis as a result of the different environments imposed by the 1,5-dioxynaphthalene unit in the linear components: Bravo, J. A.; Raymo, F. M.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Eur. J. Org. Chem.* **1998**, 2565. We thank one of the referees for reminding us of this work.

(15) In principle, the populations of the two exchange states of the tetracationic cyclophane may be different in these new hetero[3]-rotaxanes as a result of the repelling effect of the neutral cyclophane in these hetero[3]rotaxanes. However, no quantitative results could be obtained from these and previously reported (see ref 7) hetero[3]-rotaxanes because of the reduced resolution of their ^{1}H NMR at low temperature. We thank one of the referees for reminding us to pay more attention to this point.

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

compounds	λ_{max} (nm)	log ϵ (M^{-1} cm^{-1})	compounds	λ_{max} (nm)	log ϵ (M^{-1} cm^{-1})	λ_{CT} (nm)	log ϵ (M^{-1} cm^{-1})
10	286	3.85	**17**·4Cl	262	4.46	462	2.59
14a	286	3.83	**22a**·4Cl	263	4.24	467	2.58
14b	286	3.92	**22b**·4Cl	263	4.46	465	2.60
20	287	4.06	**21**·4Cl	263	4.44	464	2.42
23a	286	3.96	**24a**·4Cl	263	4.47	464	2.45
23b	286	3.91	**24b**·4Cl	263	4.37	468	2.34

subunits and the stoppers. Moreover, it can also be found that the values for all the [3]rotaxanes are remarkably lower than those of [2]rotaxaens. These results also support that greater spatial repulsions are imposed upon the tetracationic cyclophane by the neutral cyclophane in the present [3]rotaxanes, which lead to decreased donor−acceptor interaction between the pyridinium and hydroquinone subunits.

Luminescence Properties. Irradiation of the maximum absorption bands at 287 nm for the three linear molecules **10**, **14a**, and **14b** leads to emission bands with maximum at 325 nm. With the same irradiation light, emission bands are observed for neutral [2]rotaxanes **20**, **23a**, and **23b** at 326, 325, and 327 nm. However, the emission intensity of the [2]rotaxanes is remarkably reduced (50%) compared with that of the corresponding linear precursor molecules under the same measurement conditions. This quenching effect may be attributed to the result of weak interaction between the excited hydroquinone and the neutral cyclophane. Under similar conditions, no emission is detected for the hydroquinone subunits of the ionic [2]- and [3]rotaxanes because of the efficient quenching of the charge-transfer interactions.[7,9]

In summary, we have reported self-assembly and characterization of three novel hetero[3]rotaxanes, consisting of neutral and tetracationic ring components, by utilizing both intermolecular hydrogen bonding and donor−acceptor interactions. The dynamic investigation reveals that the spatial interaction between the neutral and cationic ring components of these [3]rotaxanes has been substantially increased as a result of simple relocation of the amides subunits to the central part of the linear components, which have been proved by first direct observations of NOEs between the two ring components and the reduced donor−acceptor interaction within the [3]rotaxanes. We are now using different noncovalent assembling principles to construct new functional supramolecular hybrids, which will be reported in due course.

Experimental Section

Methods and Materials. Melting points are uncorrected. ^{1}H NMR spectra were recorded on a 400 or 300 MHz spectrometer with Me_4Si as internal standard. Mass spectra were recorded in EI or ESI mode. Elemental analysis was carried out at the SIOC analytical center. Absorption spectra were recorded 20 °C. Fluorescence spectra were obtained at 20 °C. Unless stated otherwise, all reagents were obtained from commercial sources and used without further purification. The solvents have been purified by standard procedures before use. Silica gel was used for column chromatography. All reactions were carried out under an atmosphere of nitrogen.

Compound 4. To a suspension of phenol **2**[16] (10.0 g, 10.0 mmol) and K_2CO_3 (16.6 g, 40.0 mmol) in acetonitrile (150 mL) was added dibromide **3**[17] (6.63 g, 240 mmol). The mixture was then refluxed for 48 h and the solid was filtered off. The solution was concentrated and the remaining residue triturated in dichloromethane (300 mL). The solution was washed with water (2 × 50 mL) and brine (100 mL) and dried over sodium sulfate. After the solvent was removed, the residue was chromatographed (ethyl acetate/light petroleum, 1:4), to afford compound **4** as a white solid (7.32 g, 46%). Mp: 106−107 °C [lit. 102−104 °C[18]]. ^{1}H NMR ($CDCl_3$): δ 7.27−7.18 (m, 15 H), 7.10 (m, 2 H), 6.80 (m, 2 H), 4.12 (m, 2 H), 3.87−3.79 (m, 4 H), 3.71 (m, 4 H), 3.46 (t, 2 H, J = 6.3 Hz). MS (EI): m/z 530 $[M]^+$.

Compound 6. A suspension of compound **4** (4.70 g, 8.87 mmol), 4-benzoxyphenol **5** (1.80 g, 8.90 mmol), and K_2CO_3 (11.4 g, 82.6 mmol) in acetonitrile (150 mL) was refluxed for 24 h. After cooling to room temperature, the solid was filtered off and the solvent was removed. The resulting residue was worked up in a normal way and then purified by column chromatography (EtOAc/light petroleum ether, 1:3). Compound **6** was obtained as a white solid (4.48 g, 78%). Mp: 84−85 °C. ^{1}H NMR ($CDCl_3$): δ 7.43−7.37 (m, 6 H), 7.30−7.19 (m, 18 H), 7.11 (m, 2 H), 6.89−6.80 (m, 6 H), 5.02 (s, 2 H), 4.11 (m, 4 H), 3.86 (m, 4 H), 3.77 (m, 4 H). MS (EI): m/z 650 $[M]^+$. Anal. Calcd for $C_{44}H_{42}O_5$: C, 81.20; H, 6.50. Found: C, 80.74; H, 6.31.

Compound 7. Compound **6** (5.90 g, 9.08 mmol) was dissolved in methanol/methylene chloride (100 mL, 4:1), and 10% Pd−C (0.12 g) was added. The resulting mixture is stirred with bubbling of hydrogen at a pressure of 16 psi for 5 h. The catalyst was then filtered off, and the solvent was evaporated in vacuo. The crude product is purified by flash column chromatography (chloroform/methanol, 10:1). Compound **7** (4.88 g) was obtained as a white solid in 96% yield, which is recrystallized from methanol for analysis. Mp: 96−97 °C. ^{1}H NMR ($CDCl_3$): δ 7.25−7.20 (m, 15 H), 7.17 (m, 2 H), 6.78−6.71 (m, 6 H), 4.7 (b, 1 H), 4.07 (m, 4 H), 3.84 (m, 4 H), 3.80 (m, 4 H). MS (EI): m/z 560 $[M]^+$. Anal. Calcd for $C_{37}H_{36}O_5$: C, 79.26; H, 6.47. Found: C, 79.18; H, 6.51.

Compound 8. A suspension of phenol **7** (4.48 g, 8.00 mmol), methyl 4-bromobutyrate (1.44 g, 8.00 mmol), and potassium carbonate (2.24 g, 16.0 mmol) in acetonitrile (250 mL) was heated under reflux for 48 h. After cooling to room temperature, the reaction mixture was filtered. The filtrate was concentrated and the resulting residue was triturated with methylene chloride (300 mL). The resulting organic phase was washed with 2 M sodium carbonate solution (2 × 60 mL), water (60 mL), and brine (60 mL) and dried over sodium sulfate. After the solvent was removed under reduced pressure, the resulting residue was purified by chromatography (ethyl acetate/hexane, 2:3). Compound **8** was obtained as a white solid (3.44 g, 65%). Mp: 103−105 °C. ^{1}H NMR ($CDCl_3$): δ 7.15−7.26 (m, 15 H), 7.09 (d, 2 H), 6.77−6.85 (m, 6 H), 4.05−4.12 (m, 4 H), 3.93 (t, 2 H, J = 6.0 Hz), 3.81−3.86 (m, 4 H), 3.74 (s, 4 H), 3.68 (s, 3 H), 2.51 (t, 2 H; J = 7.2 Hz), 2.05−2.10 (m, 2 H). MS (EI): m/z 660 $[M]^+$. Anal. Calcd for $C_{42}H_{44}O_7$: C, 76.34; H, 6.71. Found: C, 76.10; H, 6.75.

Compound 9. This compound was obtained quantitatively as a white solid by hydrolysis of compound **9** with sodium

(16) Hart, C. *J. Am. Chem. Soc.* **1954**, *76*, 1634.

(17) Hammond, P. J.; Bell, A. P.; Hall, C. D. *J. Chem. Soc., Perkin Trans. 1* **1983**, 707.

(18) Li, Z.-T.; Stein, P. C.; Becher, J.; Jensen, D.; Mørk, P.; Svenstrup, N. *Chem. Eur. J.* **1996**, *2*, 624.

hydroxide in aqueous THF at room temperature. Mp: 79−81 °C. ^{1}H NMR ($CDCl_3$): δ 7.17−7.27 (m, 15 H), 7.09 (d, 2 H), 6.77−6.85 (m, 6 H), 4.05−4.11 (m, 4 H), 3.94 (t, 2 H, J = 6.0 Hz), 3.82−3.86 (m, 4 H), 3.74 (s, 4 H), 2.56 (t, 2 H; J = 7.2 Hz), 2.05−2.10 (m, 2 H). MS (EI): m/z 646 $[M]^+$. Anal. Calcd for $C_{41}H_{42}O_7$: C, 76.14; H, 6.55. Found: C, 75.89; H, 6.50.

Compound 10. A solution of DCC (0.89 g, 4.3 mmol), HOBt (0.58 g, 4.3 mmol), compound **9** (2.80 g, 4.30 mmol), and ethylenediamine (0.13 g, 2.2 mmol) in chloroform (150 mL) was stirred at 0 °C for 24 h. The solid was filtered off and the filtrate evaporated to give a solid residue. After workup, the resulting residue was purified by chromatography (methylene chloride/ethanol, 20:1) to give compound **10** (2.38 g, 81%) as a white powder. Mp: 112−114 °C. ^{1}H NMR ($CDCl_3$): δ 7.31−7.19 (m, 30 H), 7.10−7.07 (m, 4 H), 6.80−6.86 (m, 12 H), 6.25 (br, 2 H), 4.05−4.10 (m, 8 H), 3.83−3.89 (m, 12 H), 3.73 (m, 8 H), 3.36 (s, 4 H), 2.34 (s, 4 H), 2.05 (s, 4 H). MS (ESI): m/z 1340 $[M + Na]^+$. Anal. Calcd for $C_{84}H_{88}N_2O_{12}$: C, 76.57; H, 6.73; N, 2.13. Found: C, 76.12; H, 6.46; N, 2.22.

Compound 12. This compound was prepared as a white solid in 94% yield from the reaction of phenol **4** and *N*-(3-bromopropyl) phthalimide **11**[19] according to the procedure described above for preparing compound **12**. Mp: 41−42 °C. ^{1}H NMR ($CDCl_3$): δ 7.84 (m, 2 H), 7.71 (m, 2 H), 7.28−7.19 (m, 15 H), 7.09 (m, 2 H), 6.80 (m, 2 H), 6.79 (d, 2 H), 6.72 (m, 2 H), 4.08 (m, 4 H), 3.96 (m, 2 H), 3.87 (m, 4 H), 3.83 (m, 2 H), 3.74 (m, 4 H), 2.15 (m, 2 H). MS (EI): m/z 747 $[M]^+$. Anal. Calcd for $C_{48}H_{45}NO_7$: C, 77.09; H, 6.06; N, 1.87. Found: C, 76.70; H, 6.19; N, 2.14.

Compound 13. A mixture of phthalimide **12** (2.64 g, 3.50 mmol), benzyltriethylammonium chloride (0.80 g, 3.5 mmol), 85% hydrazine hydrate (10 mL), and chloroform (20 mL) was stirred at room temperature for 24 h and then diluted with $CHCl_3$ (200 mL). The mixture was washed with 5% aqueous NaOH solution (2 × 30 mL). After workup, the crude product was purified by flash chromatography to afford compound **13** as a white powder (1.58 g, 71%). Mp: 106−108 °C. ^{1}H NMR ($CDCl_3$): δ 7.26−7.17 (m, 17 H), 6.80 (m, 6 H), 4.11−3.73 (m, 14 H), 2.97 (m, 2 H), 1.98 (m, 2 H). MS (EI): m/z 617 $[M]^+$. Anal. Calcd for $C_{40}H_{43}NO_5 \cdot 0.5H_2O$: C, 76.71; H, 7.08; N, 2.23. Found: C, 76.48; H, 7.05; N, 2.27.

Compounds 14a and **14b** were prepared as white solids from the reactions of amine **13** with malonic acid or succinic acid, respectively, according to the method described above for preparing compound **10**. **Data for 14a**. Yield: 92%. Mp: 84−85 °C. ^{1}H NMR ($CDCl_3$): δ 7.26−7.14 (m, 30 H), 7.10−7.07 (m, 4 H), 6.84−6.76 (m, 12 H), 4.11−4.04 (m, 8 H), 3.94−3.89 (m, 4 H), 3.86−3.78 (m, 8 H), 3.73 (m, 8 H), 3.45 (s, 4 H), 3.17 (s, 1 H), 2.22 (s, 1 H), 1.94 (s, 4 H). MS (ESI): m/z 1303 (M^+). Anal. Calcd for $C_{83}H_{86}N_2O_{12} \cdot H_2O$: C, 75.43; H, 6.71; N, 2.12. Found: C, 75.56; H, 6.70; N, 2.13. **1Data for 4b**. Yield: 89%. Mp: 112−113 °C. ^{1}H NMR ($CDCl_3$): δ 7.26−7.17 (m, 30 H), 7.10−7.07 (m, 4 H), 6.84−6.76 (m, 12 H), 4.11−4.04 (m, 8 H), 3.95−3.91 (m, 4 H), 3.86−3.80 (m, 8 H), 3.74 (m, 8 H), 3.41 (m, 4 H), 2.51 (s, 4 H), 1.94 (s, 4 H). MS (ESI): m/z 1339 $[M + Na]^+$. Anal. Calcd for $C_{84}H_{88}N_2O_{12} \cdot H_2O$: C, 75.54; H, 6.79; N, 2.10. Found: C, 75.77; H, 6.68; N, 2.07.

[2]Rotaxane 17·4Cl. Compound **10** (0.70 g, 0.50 mmol), dicationic compound **15**·$2PF_6$[9] (0.12 g, 0.17 mmol), dibromide **16** (0.044 g, 0.17 mmol), and KI (20 mg) were added to DMF (30 mL). The suspension was stirred at ambient temperature for 10 days. After the solvent was removed under reduced pressure, and the residue was washed with ether and then subjected to column chromatography. $CHCl_3$/EtOH (10:1) was first used as eluent to elute the neutral compounds, and then MeOH/$MeNO_2$/NH_4Cl (2 N aqueous solution) (7:1:2) was used as eluent. The orange fractions were collected and combined. The solvent was removed under reduced pressure. The residue was washed with cold water completely to give [2]rotaxane **17**·4Cl (0.34 g, 34%) as a orange solid, which was purified further by recrystallization from MeOH. Mp: 204−208 °C (dec). ^{1}H NMR (CD_3OD): δ 9.28 (s, 8 H,), 8.23 (s, 8 H), 7.93 (s, 8 H), 6.92−7.20 (m, 34 H), 6.40−6.78 (m, 8 H), 5.82 (s, 8 H), 3.30−4.07 (m, 28 H), 2.50 (m, 4 H), 2.07 (m, 4 H), 1.29 (s, 4 H). MS (ESI): m/z 955 $[M - 2Cl]^{2+}$, 1285 $[2M - 3Cl]^{3+}$. Anal. Calcd for $C_{120}H_{120}Cl_4N_6O_{12}$: C, 72.79; H, 6.11; N, 4.24. Found: C, 72.41; H, 6.09; N, 4.18.

[2]Rotaxane 20. To a stirred solution of compound **10** (1.32 g, 1.00 mmol) and triethylamine (2.76 mL, 20.0 mmol) in chloroform (50 mL) were added with stirring a solution of *m*-phthaloyl dicholoride **18** (0.20 g, 1.00 mmol) in chloroform (50 mL) and a solution of *p*-xylylene diamine **19** (0.14 g, 1.00 mmol) in chloroform (50 mL) at room temperature simultaneously over 5 h. 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 × 10 mL), 5% $NaHCO_3$ solution (3 × 10 mL), water (10 mL), and brine (10 mL) and then dried over sodium sulfate. The solvent was evaporated in vacuo, and the resulting residue was purified by flash chromatography ($CHCl_3$/MeOH, 20:1). [2]Rotaxane **20** (0.63 g, 34%) was obtained as a white solid. Mp: 144−145 °C. ^{1}H NMR ($CDCl_3$): δ 8.16 (s, 2 H), 8.07 (d, 4 H, J = 7.5 Hz), 7.56 (br, 4 H), 7.47 (t, 2 H, J = 7.5 Hz), 7.27−7.14 (m, 40 H), 7.05 (d, 2 H, J = 8.7 Hz), 6.71−6.52 (m, 12 H), 4.50 (s, 8 H), 3.97−3.99 (m, 8 H), 3.73−3.69 (s, 20 H), 3.10 (s, 4 H), 1.95 (s, 4 H), 1.69 (s, 4 H). Anal. Calcd for $C_{115}H_{114}N_6O_{16} \cdot H_2O$: C, 74.49; H, 6.31; N, 4.53. Found: C, 74.79; H, 6.74; N, 4.38.

[3]Rotaxane 21·4Cl. This [3]rotaxane was prepared in 31% yield as a red solid from the reaction of compounds **15**·$2PF_6$ and **16** in the presence of [2]rotaxane **20** by using a similar procedure as described for preparing **17**·4Cl. Mp: 220−225 °C (decom.). ^{1}H NMR (DMSO-d_6): δ 9.91 (s, 4 H), 9.85 (s, 4 H), 9.62 (s, 4 H), 8.83 (s, 4 H), 8.50 (s, 4 H), 8.16 (s, 2 H), 8.11 (m, 4 H), 8.03 (s, 8 H), 7.64 (m, 2 H), 6.78−7.34 (m, 50 H), 5.85−6.06 (m, 8 H), 4.92−4.97 (m, 4 H), 4.24−4.27 (m, 4 H), 3.30−4.03 (m, 28 H), 2.87−3.01 (m, 4 H), 2.30 (s, 4 H), 2.12 (s, 4 H), 1.91 (s, 4 H). MS (ESI): m/z 592 $[M - 4Cl]^{4+}$, 802 $[M - 3Cl]^{3+}$, 1221 $[M - 2Cl]^{2+}$. Anal. Calcd for $C_{152}H_{148}Cl_4N_{10}O_{16} \cdot 4H_2O$: C, 70.63; H, 6.08; N, 5.42. Found: C, 70.63; H, 6.53; N, 4.99.

[2]Rotaxane 22a·4Cl was prepared in 37% yield as a red solid from the reaction of compounds **15**·$2PF_6$ and **16** in the presence of **14a** by using a similar procedure as described above for preparing **17**·4Cl. Mp: 168−170 °C. ^{1}H NMR (CD_3OD): δ 9.24 (s, 8 H), 8.23 (s, 8 H), 7.23−6.92 (m, 34 H), 6.42−6.77 (m, 8 H), 4.90−5.85 (m, 8 H), 3.30−4.09 (m, 34 H), 2.12 (s, 2 H), 1.79 (s, 2 H), 1.27 (s, 4 H), 0.89 (s, 2 H). MS (ESI): m/z 456 $[M - 4Cl]^{4+}$, 619 $[M - 3Cl]^{3+}$, 947 $[M - 2Cl]^{2+}$. Anal. Calcd for $C_{119}H_{118}Cl_4N_6O_{12} \cdot 2H_2O$: C, 71.39; H, 6.14; N, 4.20. Found: C, 71.16; H, 6.23; N, 4.13.

[2]Rotaxane 22b·4Cl was prepared in 33% yield as a red solid from the reaction of compounds **15**·$2PF_6$ and **16** in the presence of **14b** by using a similar procedure as described above for preparing **17**·4Cl. Mp: 202−207 °C (dec). ^{1}H NMR (CD_3OD): δ 9.25 (s, 8 H), 8.23 (s, 8 H), 7.20−6.92 (m, 34 H), 6.43−6.78 (m, 8 H), 5.81 (m, 8 H), 3.21−4.09 (m, 36 H), 2.63 (s, 4 H), 2.09 (s, 2 H), 1.79 (s, 2 H), 1.27 (s, 2 H). MS (ESI): m/z 955 $[M - 2Cl]^{2+}$. Anal. Calcd for $C_{120}H_{120}Cl_4N_6O_{12} \cdot 2H_2O$: C, 71.49; H, 6.20; N, 4.17. Found: C, 71.14; H, 6.27; N, 4.14.

[2]Rotaxanes 23a and 23b were prepared as white solids in 26% and 28% yields, respectively, from the reaction of **18** with **19** in the presence of **14a** or **14b** by using a similar procedure as described for preparing [2]rotaxane **20**. **Data for 23a**. Mp: 103−105 °C. ^{1}H NMR ($CDCl_3$): δ 8.41 (s, 2 H), 8.24 (d, 4 H, J = 6.7), 7.65 (m, 6 H), 7.17−7.63 (m, 42 H), 6.75−6.88 (m, 12 H), 4.60 (s, 8 H), 4.07−4.16 (s, 8 H), 3.76−3.92 (s, 20 H), 3.31 (s, 4 H), 2.33 (s, 2 H), 1.90 (s, 4 H). MS (ESI): m/z 1837 $[M]^+$. Anal. Calcd for $C_{115}H_{114}N_6O_{16} \cdot H_2O$: C, 74.49; H, 6.31; N, 4.53. Found: C, 74.29; H, 6.32; N, 4.39. **Data for 23b**. Mp: 144−146 °C. ^{1}H NMR ($CDCl_3$): δ 8.36 (s, 2 H), 8.16 (d, 4 H, J = 7.2), 7.65 (br, 4 H), 7.56 (t, 2 H), 7.06−7.28 (m, 42 H), 6.66−6.76 (m, 12 H), 4.49 (s, 8H), 3.68−4.14 (s, 28H), 3.29 (s,

(19) Amundsen, S. *Org. Synth*. **1944**, *24*, 46.

4H), 1.90 (s, 4H), 1.35 (s, 4H). MS (ESI): *m*/*z* 1850 $[M]^+$. Anal. Calcd for $C_{116}H_{116}N_6O_{16}\cdot H_2O$: C, 75.30; H, 6.32; N, 4.54. Found: C, 75.07; H, 6.42; N, 4.46.

[3]Rotaxanes 24a·4Cl and 24b·4Cl were prepared as red solids in 41% and 40% yields, respectively, from the reactions of **15**·2PF_6 with **16** in the presence of [2]rotaxanes **23a** or **23b** by using a similar procedure as described for preparing **17**·4Cl. **Data for 24a**·4Cl. Mp: 213−217 °C (dec). ^{1}H NMR (DMSO-d_6): δ 9.89 (s, 4 H), 9.85 (s, 4 H), 9.55 (s, 4 H), 8.80 (s, 4 H), 8.63 (s, 4 H), 8.21 (s, 2 H), 8.50 (m, 4 H), 8.00 (s, 8 H), 7.66 (m, 2 H), 6.65−7.32 (m, 50 H), 5.93 (s, 8 H), 4.93−4.96 (m, 4 H), 4.23−4.26 (m, 4 H), 3.31−4.02 (m, 28 H), 2.89−2.99 (m, 4 H), 2.67 (s, 2 H), 2.12 (s, 4 H), 1.82 (s, 2 H), 1.23 (s, 4 H). MS (ESI): *m*/*z* 797 $[M - 3Cl]^{3+}$, 1214 $[M - 2Cl]^{2+}$. Anal. Calcd for $C_{151}H_{146}Cl_4N_{10}O_{16}\cdot 4H_2O$: C, 70.55; H, 6.04; N, 5.45. Found: C, 70.78; H, 6.12; N, 5.57. **24b**·4Cl. Mp: 226−229 °C (dec). ^{1}H NMR (DMSO-d_6): δ 9.86 (s, 4 H), 9.84 (s, 4 H), 9.53 (s, 4 H), 8.80 (s, 4 H), 8.62 (s, 4 H), 8.22 (s, 2 H), 8.50 (m, 4 H), 8.00 (s, 8 H), 7.66 (m, 2 H), 6.65−7.33 (m, 50 H), 5.93 (s, 8 H), 4.93−4.96 (m, 4 H), 4.23−4.26 (m, 4 H), 3.30−4.03 (m, 28 H), 2.89−2.99 (m, 4 H), 2.73 (s, 2 H), 2.18 (s, 4 H), 1.89 (s, 2 H), 1.53 (s, 4 H). MS (ESI): *m*/*z* 593 $[M - 4Cl]^{4+}$, 802 $[M - 3Cl]^{3+}$, 1221 $[M - 2Cl]^{2+}$. Anal. Calcd for $C_{152}H_{148}Cl_4N_{10}O_{16}\cdot 2H_2O$: C, 71.62; H, 6.02; N, 5.50. Found: C, 71.24; H, 5.83; N, 5.27.

Acknowledgment. This work was financially supported by the NSFC and the Ministry of Science and Technology of China. We thank Professors Ji-Liang Shi and Min Shi for beneficial discussions.

Supporting Information Available: Temperature dependent ^{1}H NMR spectra of compounds **17**·4Cl, **21**·4Cl, **22a**·4Cl, **22b**·4Cl, **24a**·4Cl, and **24b**·4Cl. This material is available free of charge via the Internet at http://pubs.acs.org.

JO026370I