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Size effects in the alkali metal ion-templated formation of oligo(ethylene glycol)-containing [2]catenanes†

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An investigation into the most suitable alkali metal ions for templating the assembly of [2]catenanes from di-, tri-, and tetra(ethylene glycol)-containing guest diamines and isophthalaldehyde has indicated that Na^+, K^+, and Rb^+ ions are optimal for preparing [2]catenanes containing at least one di(ethylene glycol) unit, two tri(ethylene glycol) units, and at least one tetra(ethylene glycol) unit [in the absence of a di(ethylene glycol) unit], respectively.

Introduction

A template aligns its bound species in a manner that facilitates the efficient synthesis of a particular product.[1] Because of their strong interactions with ligands containing nitrogen, oxygen, and sulfur atoms, transition metal ions have, for over five decades, been applied to template the syntheses of planar macrocycles containing such heteroatoms.[2] By aligning two (or more) pyridine-type ligands into a polyhedral configuration, transition metal ions can also be useful templates for the construction of aesthetically appealing interlocked molecules and molecular knots[3] (*e.g.*, trefoil knots,[4] Borromean rings,[5] Stars of David[6]). Although alkali metal ions have also been applied for many years to template the syntheses of crown ethers,[7] they have rarely been employed as templates to direct the syntheses of interlocked molecules.[8] Recently, we found that the Na^+ ion can template the orthogonal alignment of two di(ethylene glycol) chains, allowing the direct construction of a [2]catenane through the assembly of five components [two di(ethylene glycol)-containing diamines, two isophthalaldehydes, one Na^+ ion].[9] To explore the possible applications of [2]catenanes synthesized using this approach, we wished to investigate its synthetic flexibility by replacing one (or both) of the Na^+ ion-aligned di(ethylene glycol) units with a longer analogue, providing hetero-[2]catenanes (two nonequivalent macrocyclic components) or larger homo-[2]catenanes. We suspected, however, that efficient alignment of the longer analogues of the di(ethylene glycol) units would require other alkali metal ions as templates, suggesting the need for a systematic study to find the best alkali metal ion for templating each possible homo- and hetero-[2]catenane assembled in this way. Herein, we report the results of our investigation into the use of different alkali metal ions to template the assembly of [2]catenanes from di-, tri-, and tetra(ethylene glycol)-containing guest diamines and isophthalaldehyde. We found that Na^+ is the best alkali metal ion to template the assembly of [2]catenanes containing di(ethylene glycol) units, with K^+ being the best choice only for the construction of a tri(ethylene glycol)-containing homo-[2]catenane. When the assembly involved the tetra(ethylene glycol)-containing diamine **3**, but not the di(ethylene glycol)-containing diamine **1**,[9] Rb^+ became the templating ion providing the most efficient assembly.

Results and discussion

To investigate the template effects in the syntheses of a variety of [2]catenanes, we synthesized the diamines **1–3**, containing central di-, tri-, and tetra(ethylene glycol) motifs, respectively, by reacting the corresponding oligo(ethylene glycol)s with 4-cyanobenzylbromide under basic conditions to give the nitriles **4–6**, respectively, and then reducing them with $LiAlH_4$ (Scheme 1).

First, we examined the syntheses of the homo-[2]catenanes, because only one possible [2]catenane could be generated in each solution. Thus, we heated $CDCl_3$ solutions of the di(ethylene glycol)-containing diamine **1** (20 mM), the dialdehyde **7** (20 mM), and alkali metal ions in the form of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) salts (10 mM) at 323 K until the reactions reached equilibrium (generally 24 h)

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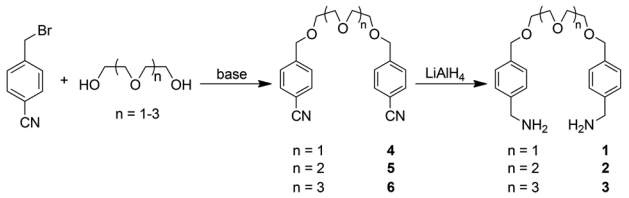


Scheme 1 Syntheses of diamines **1–3**.

(Scheme 2). Only the mixtures in which Li^+ and Na^+ ions were present displayed the characteristic xylene-shielded upfield signals (δ 2.50–3.10)[9] for the protons of the ethylene glycol units in the ^{1}H NMR spectra, indicating the formation of their [2]catenanes [**8**·Li]$^+$ and [**8**·Na]$^+$, respectively (Fig. 1A). With integration of the signal for the TFPB anion at δ 7.70 as a reference, the yields of the [2]catenanes [**8**·Na]$^+$ and [**8**·Li]$^+$ were 81 and 55%, respectively (Table 1). Because Na^+ and K^+ ions can be difficult to differentiate,[10] our observation that the [2]catenane [**8**·M]$^+$ can be synthesized efficiently when using Na^+ ions, but not K^+ ions, as templates suggests an alternative method for discerning between these two metal ions. We suspect that the inability of K^+ and other larger alkali metal ions to template the formation of their [2]catenanes [**8**·M]$^+$ arose from the binding pocket formed from the two orthogonally aligned di(ethylene glycol) chains being too small to host these cations appropriately.

Similar to the significantly upfield-shifted signals for the xylene-shielded di(ethylene glycol) units in the ^{1}H NMR spectrum of the homo-[2]catenane [**8**·Na]$^+$, the spectra of the $CDCl_3$ solutions of the tri(ethylene glycol)-containing diamine **2** (20 mM), the dialdehyde **7** (20 mM), and alkali metal ions in the form of their TFPB salts (10 mM), after heating at 323 K for 24 h, all featured three characteristic upfield-shifted signals at δ 2.90–3.40, representing the xylene-shielded tri(ethylene glycol) units in the homo-[2]catenanes [**9**·M]$^+$.

This observation suggested that all of the tested alkali metal ions were capable of templating the formation of the homo-[2]catenanes [**9**·M]$^+$, although their efficiencies varied significantly. We estimated the yields of the [2]catenanes [**9**·M]$^+$ assembled using the various alkali metal ions as templates by comparing the integrated signals of the tri(ethylene glycol) and/or benzylic protons of each [2]catenane (δ 2.90–3.40 and 4.21, respectively) with the signal of the TFPB anions (δ 7.70). The K^+ ion appeared to be the best template (yield: 75%). The smallest ion (Li^+, 7%) and the largest (Cs^+, 25%) were both much less efficient templates for the assembly of their [2]catenanes [**9**·M]$^+$. This finding suggests that when the two oligo(ethylene glycol) chains were aligned orthogonally for the synthesis of the [2]catenanes, the binding pocket that formed preferred a specifically size-matched template.

Because K^+ was the best alkali metal ion for templating the assembly of the tri(ethylene glycol)-containing homo-[2]catenane [**9**·M]$^+$, whereas the smaller Na^+ ion was much better at templating the formation of [**8**·M]$^+$ with two shorter di(ethylene glycol) chains, we suspected that obtaining the [2]catenane [**10**·M]$^+$, formed from two units of the tetra(ethylene glycol)-containing diamine **3** and the dialdehyde **7**, would prefer an alkali metal ion larger than K^+ as the template. Fig. 1C presents the ^{1}H NMR spectra of the $CDCl_3$ solutions of the diamine **3** (20 mM), the dialdehyde **7** (20 mM), and alkali metal ions in the form of TFPB salts (10 mM), recorded after heating at 323 K for 24 h. The spectra displayed the four characteristic upfield-shifted signals of the interlocked tetra

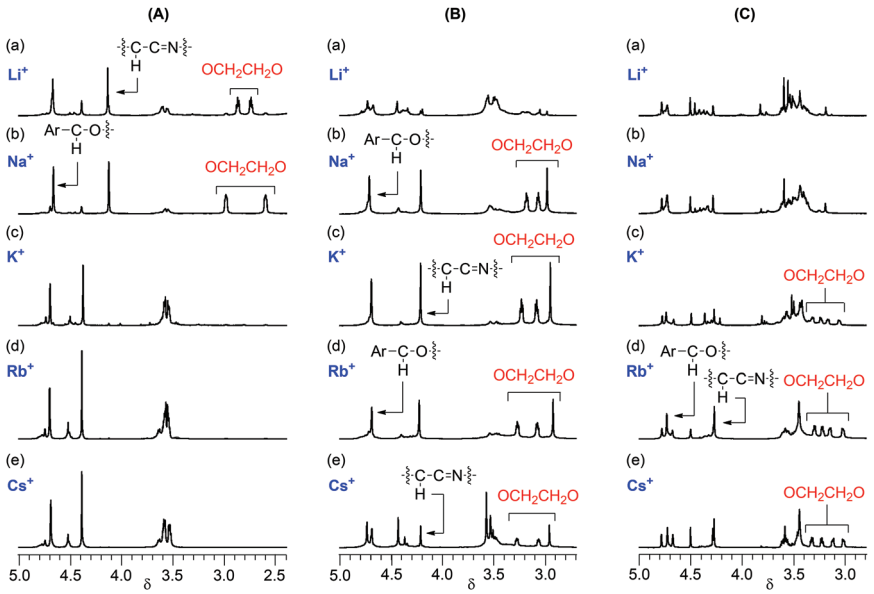
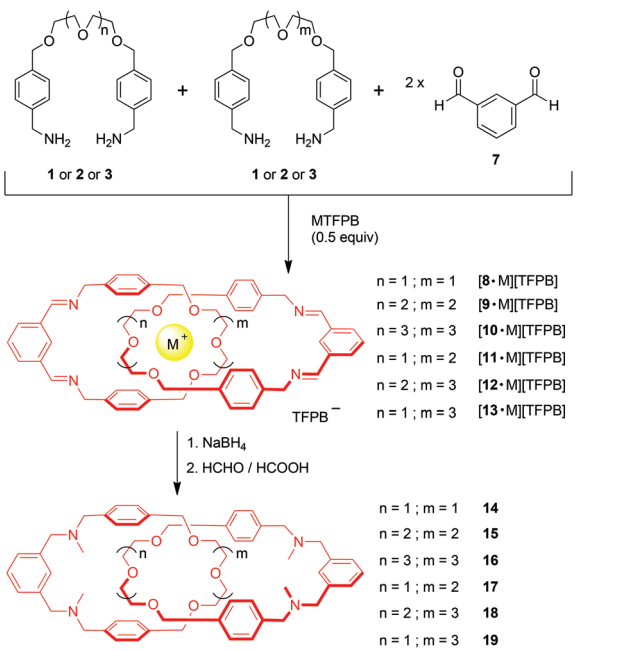


Fig. 1 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the mixtures of the dialdehyde **2**, M^+TFPB^- salts, and the diamines (A) **1**, (B), **2** and (C) **3**, where the M^+ ions were (a) Li^+, (b) Na^+, (c) K^+, (d) Rb^+, and (e) Cs^+.

Table 1 Estimated yields (from ^{1}H NMR spectra) of the [2]catenanes [**8**·M]$^+$–[**13**·M]$^+$ assembled from the diamines **1–3** and the dialdehyde **7** when using various alkali metal ions as templates

Template	Diamines	**8**	**9**	**10**	**11**	**12**	**13**
Li^+	**1** + **1**	55%	—	—	—	—	—
Na^+	**1** + **1**	81%	—	—	—	—	—
K^+	**1** + **1**	0%	—	—	—	—	—
Rb^+	**1** + **1**	0%	—	—	—	—	—
Cs^+	**1** + **1**	0%	—	—	—	—	—
Li^+	**2** + **2**	—	7%	—	—	—	—
Na^+	**2** + **2**	—	64%	—	—	—	—
K^+	**2** + **2**	—	75%	—	—	—	—
Rb^+	**2** + **2**	—	57%	—	—	—	—
Cs^+	**2** + **2**	—	28%	—	—	—	—
Li^+	**3** + **3**	—	—	0%	—	—	—
Na^+	**3** + **3**	—	—	0%	—	—	—
K^+	**3** + **3**	—	—	19%	—	—	—
Rb^+	**3** + **3**	—	—	42%	—	—	—
Cs^+	**3** + **3**	—	—	26%	—	—	—
Li^+	**1** + **2**	16%	ND[a]	—	ND[a]	—	—
Na^+	**1** + **2**	18%	21%	—	19%	—	—
K^+	**1** + **2**	0%	36%	—	ND[a]	—	—
Rb^+	**1** + **2**	0%	31%	—	ND[a]	—	—
Cs^+	**1** + **2**	0%	11%	—	ND[a]	—	—
Li^+	**2** + **3**	—	2%	0%	—	ND[a]	—
Na^+	**2** + **3**	—	14%	0%	—	ND[a]	—
K^+	**2** + **3**	—	12%	8%	—	9%	—
Rb^+	**2** + **3**	—	16%	12%	—	11%	—
Cs^+	**2** + **3**	—	5%	11%	—	4%	—
Li^+	**1** + **3**	8%	—	ND[a]	—	—	ND[a]
Na^+	**1** + **3**	11%	—	ND[a]	—	—	ND[a]
K^+	**1** + **3**	0%	—	3%	—	—	ND[a]
Rb^+	**1** + **3**	0%	—	13%	—	—	ND[a]
Cs^+	**1** + **3**	0%	—	7%	—	—	ND[a]

[a] Not determined because no reliable signal was observed.



Scheme 2 Template-directed synthesis of the [2]catenanes [(**8–13**)·M]$^+$ and **14–19**.

(ethylene glycol) units in the [2]catenanes [**10**·M]$^+$ only when we applied K^+, Rb^+, and Cs^+ ions as templates. Among them, the Rb^+ ion is the most efficient template for the synthesis of the [2]catenanes [**10**·M]$^+$, although the yield of its product (42%) was significantly lower than those determined similarly for the formation of the [2]catenanes [**8**·Na]$^+$ and [**9**·K]$^+$ (81 and 75%, respectively). We suspect that the entropic cost when organizing the two highly flexible tetra(ethylene glycol) chains into the complexation geometry as well as the lower enthalpy when coordinating the oxygen atoms of the tetra(ethylene glycol) units to the lower-charge-density Rb^+ ion were responsible for the relatively low efficiency of this transformation. The inability of Na^+ ions to template the formation of the relatively large tetra(ethylene glycol)-containing [2]catenane [**10**·M]$^+$ and the inability of K^+ ions to template the formation of the relatively small di(ethylene glycol)-containing [2]catenane [**8**·M]$^+$ suggest an alternative method of differentiating between these two alkali metal ions when they are the only ones present in solution.

To prove unambiguously that the homo-[2]catenanes [(**8–10**)·M]$^+$ formed in solution, we heated mixtures of the diamines **1–3**, the dialdehyde **7**, and their best templating ions (as determined above) at 323 K for 24 h and then reduced the products with $NaBH_4$. We then methylated (HCHO/HCOOH) the resulting secondary amino groups to afford the [2]catenanes **14–16**.[11] After chromatography, we isolated the di- and tri(ethylene glycol)-containing homo-[2]catenanes **14** and **15**, respectively, in moderate yields (58 and 48%, respectively), confirming that Na^+ and K^+ ions are efficient templates for the assembly of the imino [2]catenanes [**8**·Na]$^+$ and [**9**·K]$^+$. Because of the lower efficiency (42%) of the Rb^+-templated formation of the imino [2]catenane [**10**·M]$^+$, the isolated yield of the amino [2]catenane **16** was only 30% (Table 2). The templating alkali metal ions were lost at some point during the aqueous extraction and chromatography processes (possibly because their complexation to the binding pocket in the [2]catenanes was not particularly strong), as evidenced by the ^{1}H NMR spectra of the purified [2]catenanes **14–16** lacking any signals from the TFPB counter anions.

Having assigned the signals of the homo-[2]catenanes **14–16** in their ^{1}H NMR spectra, we could identify the signals of the hetero-[2]catenanes **17–19** in the ^{1}H NMR spectra of the structures assembled when mixing two different diamines (chosen from **1–3**), the dialdehyde **7**, and M·TFPB salts (Fig. 2).

Table 2 Isolated yields of the [2]catenanes **14–19** assembled from the diamines **1–3** and the dialdehyde **7** when using the most-suitable alkali metal ion as the template in each case

Template	Diamines	**14**	**15**	**16**	**17**	**18**	**19**
Na^+	**1** + **1**	58%	—	—	—	—	—
K^+	**2** + **2**	—	48%	—	—	—	—
Rb^+	**3** + **3**	—	—	30%	—	—	—
Na^+	**1** + **2**	21%	24%	—	16%	—	—
Rb^+	**2** + **3**	—	16%	26%	—	16%	—
Na^+	**1** + **3**	19%	—	1%	—	—	6%

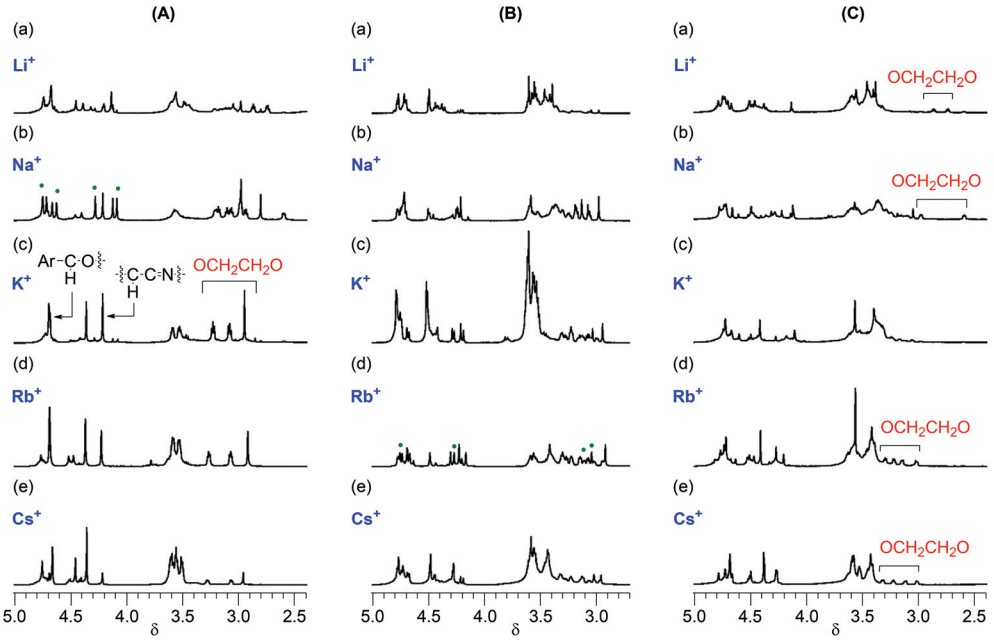


Fig. 2 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of the mixtures of the dialdehyde **7**, M^+TFPB^- salts, and the diamines (A) **1** and **2**, (B) **2** and **3**, and (C) **1** and **3**, where the M^+ ions were (a) Li^+, (b) Na^+, (c) K^+, (d) Rb^+, and (e) Cs^+. Asterisks: signals assigned to the hetero-[2]catenanes.

For example, after heating a mixture of the diamines **1** (10 mM) and **2** (10 mM), the dialdehyde **7** (20 mM), and alkali metal ions in the form of their TFPB salts (10 mM) in $CDCl_3$ at 323 K for 24 h, the ^{1}H NMR spectrum of the reaction templated by Na^+ ions was the only one to feature a reasonably intense new set of signals corresponding to the hetero-[2]catenane $[\mathbf{11}\cdot M]^+$. A tiny set of signals, similar to those assigned for the hetero-[2]catenane $[\mathbf{11}\cdot Na]^+$, appeared in the ^{1}H NMR spectrum when using the K^+ ion as the template, suggesting that the latter ion remained too large to template the formation of $[\mathbf{11}\cdot K]^+$ efficiently; instead, the predominant interlocked species in solution was the better-complexed homo-[2]catenane $[\mathbf{9}\cdot K]^+$. As expected, Rb^+ and Cs^+ ions, both larger than a K^+ ion, were not capable of templating the formation of their hetero-[2]catenanes $[\mathbf{11}\cdot M]^+$, giving their tri(ethylene glycol)-containing homo-[2]catenanes $[\mathbf{9}\cdot M]^+$ as the only interlocked products. The smallest ion, Li^+, which did not template the formation of the homo-[2]catenane $[\mathbf{9}\cdot Li]^+$, was again too small to align one unit of di(ethylene glycol) with one of tri(ethylene glycol) for the assembly of the hetero-[2]catenane $[\mathbf{11}\cdot Li]^+$. Because Na^+ is the best template for the formation of the hetero-[2]catenane $[\mathbf{11}\cdot M]^+$, we heated a $CHCl_3$ solution of the diamines **1** and **2**, the dialdehyde **7**, and NaTFPB at 323 K for 24 h, reduced the imino bonds with $NaBH_4$, and then methylated (HCHO/HCOOH) the resulting secondary amino groups in the [2]catenane. After chromatographic purification, we isolated the hetero-[2]catenane **17** and the homo-[2]catenanes **14** and **15** in yields of 16, 21, and 24%, respectively. Although the various intermediates may have had different stabilities under these reduction conditions, the isolated yields of **14** (21%), **15** (24%), and **17** (16%) did not deviate much from those estimated from the ^{1}H NMR spectrum of their imino-[2]catenane precursors $[\mathbf{8}\cdot Na]^+$ (18%), $[\mathbf{9}\cdot Na]^+$ (21%), and $[\mathbf{11}\cdot Na]^+$ (19%), respectively.

The Rb^+ ion is the best template among our tested alkali metal ions when assembling the hetero-[2]catenane $[\mathbf{12}\cdot M]^+$ from the tri(ethylene glycol)-containing diamine **2** and the tetra(ethylene glycol)-containing diamine **3**. Although K^+ and Cs^+ ions also templated the formation of their same [2]catenanes $[\mathbf{12}\cdot M]^+$, they more strongly preferred to template the assembly of their homo-[2]catenanes $[\mathbf{9}\cdot K]^+$ and $[\mathbf{10}\cdot Cs]^+$, respectively. After using $NaBH_4$ to reduce the imino bonds of the hetero-[2]catenane $[\mathbf{12}\cdot Rb]^+$ [generated from a solution of the diamines **2** (10 mM) and **3** (10 mM), the dialdehyde **7** (20 mM), and RbTFPB (10 mM) in $CDCl_3$] and methylating the resulting secondary amino groups, we isolated the hetero-[2]catenane **18** in 16% yield as well as the homo-[2]catenanes **15** and **16**, in yields of 26 and 16%, respectively, confirming that the Rb^+ ion is a suitable template for the formation of this hetero-[2]catenane.

The formation of the hetero-[2]catenanes $[\mathbf{13}\cdot M]^+$ was the most challenging because the synthesis required a short di(ethylene glycol) unit and a long tetra(ethylene glycol) unit to be aligned by a single alkali metal ion, with unavoidable competition from the formation of the homo-[2]catenanes $[\mathbf{8}\cdot M]^+$ and $[\mathbf{10}\cdot M]^+$. The ^{1}H NMR spectra of the mixtures of the diamines **1** (10 mM) and **3** (10 mM), the dialdehyde **7** (20 mM), and alkali metal ions in the form of their TFPB salts (10 mM), after heating at 323 K for 24 h, displayed no convincing sets of signals corresponding to the hetero-[2]catenanes $[\mathbf{13}\cdot M]^+$. The homo-[2]catenane $[\mathbf{8}\cdot M]^+$ was preferred in the presence of the smaller Li^+ and Na^+ ions, while the homo-[2]catenane $[\mathbf{10}\cdot M]^+$

Table 3 Binding constants and thermodynamic data for the interactions between the [2]catenanes **14–19** and their optimal templating alkali metal ions[a]

Host	Metal ion	K [M^{-1}]	$\Delta G°$ [kcal M^{-1}]	$\Delta H°$ [kcal M^{-1}]	$\Delta S°$ [cal K^{-1} M^{-1}]
18C6	Na^+	$(2.6 \pm 0.8) \times 10^6$	-8.8 ± 0.2	-2.4 ± 0.1	21.2 ± 3.0
18C6	K^+	$(2.1 \pm 0.6) \times 10^6$	-8.6 ± 0.2	-7.0 ± 0.1	5.2 ± 1.3
14	Na^+	$(3.8 \pm 0.9) \times 10^5$	-7.6 ± 0.2	-4.2 ± 0.1	11.3 ± 0.9
15	K^+	$(1.7 \pm 0.3) \times 10^6$	-8.5 ± 0.1	-6.3 ± 0.1	7.1 ± 1.3
16	Rb^+	$(9.2 \pm 1.0) \times 10^5$	-8.1 ± 0.1	-8.4 ± 0.1	-0.8 ± 0.9
17	Na^+	$(3.3 \pm 0.6) \times 10^5$	-7.5 ± 0.1	-4.8 ± 0.1	9.1 ± 2.5
18	Rb^+	$(6.8 \pm 0.9) \times 10^5$	-8.0 ± 0.1	-7.6 ± 0.1	1.2 ± 1.1
19	Na^+	$(3.0 \pm 0.4) \times 10^5$	-7.5 ± 0.1	-4.9 ± 0.1	8.7 ± 1.5

[a] Each value is the average from three independent experiments.

was preferred when applying the larger Rb^+ and Cs^+ ions, confirming that cross alignment of the two different amines was unfavorable under these conditions. Nevertheless, because the ^1H NMR spectra of the solutions containing Na^+ and K^+ ions as templates were relatively complicated, we subjected their mixtures to reduction ($NaBH_4$) and methylation (HCHO/HCOOH) in the hope that we could isolate the amino hetero-[2]catenane **19** to confirm the formation of the imino hetero-[2]catenanes [**13**·M]$^+$ in solution. Gratifyingly, we isolated the hetero-[2]catenane **19** in 6% yield from the solution containing Na^+ as the template; in contrast, the mixture in which K^+ was the template afforded only a trace amount of the hetero-[2]catenane **18**. Thus, the Na^+ ion is the best alkali metal ion for templating the formation of the di- and tetra(ethylene glycol)-containing hetero-[2]catenane [**13**·M]$^+$.

We used isothermal titration calorimetry (ITC) to determine the association constants and thermodynamic constants for the interactions of the [2]catenanes **14–19** with their most suitable templating alkali metal ions in a mixture of CH_2Cl_2 and CH_3CN (7 : 3). The binding constants of the [2]catenanes **14** and **15** to Na^+ and K^+ ions, respectively, were comparable to those of [18]crown-6 to these two alkali metal ions under the same conditions (Table 3). Thus, although the two orthogonally aligned oligo(ethylene glycol) chains in the [2]catenanes **14** and **15** are not covalently linked, their interlocking allows them to operate cooperatively as very good binders of alkali metal ions. Also with six oxygen atoms in the binding pocket, the [2]catenane **14** is enthalpically more favorable than [18]crown-6 in the binding of a Na^+ ion, suggesting that the orthogonal alignment of the two di(ethylene glycol) units allows the oxygen atoms to better interact with the Na^+ ion than does the planar cyclic arrangement. Nevertheless, the structural flexibility of the [2]catenane **14** is greater than that of [18]crown-6, resulting in higher entropy loss when organizing the former's binding pocket for complexation of the Na^+ ion; accordingly, the entropy of binding a Na^+ ion to [18]crown-6 is significantly larger than that to the [2]catenane **14**, making the binding affinity of the Na^+ ion to the latter slightly stronger than that to the former. For the K^+ ion, the best-fitting alkali metal ion to [18]crown-6, the situation is different. The complexation of a K^+ ion to [18]crown-6 is enthalpically slightly more favorable and entropically slightly less favorable than those for its complexation to the [2]catenane **15**, implying only slight differences in their host binding pockets. We measured greater enthalpy gains for the complexation of the [2]catenanes **14–16** to their optimal templating Na^+, K^+, and Rb^+ ions, respectively, consistent with the fact that the binding of more-sizable cations in larger binding pockets with higher numbers of oxygen atoms is enthalpically more favorable. Because higher entropy losses were, however, required to organize these longer oligo(ethylene glycol) chains into their binding pockets, the binding affinities of the [2]catenanes **14–16** to their optimal templating alkali metal ions did not deviate too much. Interestingly, the complexation of Na^+ ions to the di(ethylene glycol)-containing [2]catenanes **14**, **17**, and **19** occurred with very similar binding enthalpies and entropies, implying that the sizes and shapes of the binding pockets induced by the Na^+ ions were quite similar, regardless of the length of the oligo(ethylene glycol) chain in the other macrocyclic component.

Conclusions

We have determined the most suitable alkali metal ions for templating the assembly of various homo- and hetero-[2]catenanes from the diamines **1–3** and the dialdehyde **7**. We conclude that Na^+ is the best templating ion among the tested alkali metal ions for constructing [2]catenanes containing di(ethylene glycol) units, namely the homo-[2]catenane [**8**·M]$^+$ and the hetero-[2]catenanes [**11**·M]$^+$ and [**13**·M]$^+$. For [2]catenanes featuring tetra(ethylene glycol), but not di(ethylene glycol), units, namely the homo-[2]catenane [**10**·M]$^+$ and the hetero-[2]catenane [**12**·M]$^+$, Rb^+ is the best template among our tested alkali metal ions. For construction of the homo-[2]catenane [**9**·M]$^+$, K^+ is the best template for aligning its two tri(ethylene glycol) units. Thus, it is possible to assemble a variety of [2]catenanes from oligo(ethylene glycol)-containing diamines and isophthalaldehyde after judicious selection of a suitable alkali metal ion as the template. The ability to construct such [2]catenanes with differently sized macrocyclic units should assist in the development of interesting inter-

locked switches; indeed, we are now investigating the dynamic behavior and switching properties of these [2]catenanes.

Experimental

General

All glassware, stir bars, syringes, and needles were either oven- or flame-dried prior to use. All reagents, unless otherwise indicated, were obtained from commercial sources. Reactions were conducted under N_2 or Ar atmospheres. Thin layer chromatography (TLC) was performed on Merck 0.25 mm silica gel (Merck Art. 5715). Column chromatography was performed using Kieselgel 60 (Merck, 70–230 mesh) and Chromatorex NH series (Fuji Silysia, MB100-40/75). Melting points were determined using a Fargo MP-2D melting point apparatus. For NMR spectroscopy, the deuterated solvent was used as the lock and the solvent's residual protons were employed as the internal standard.

Benzonitrile 5. NaH (1.34 g, 56.0 mmol) was added to a solution of tri(ethylene glycol) (3.00 mL, 22.4 mmol) in THF (224 mL) and then the mixture was stirred at room temperature for 30 min. After the addition of 4-cyanobenzylbromide (11.0 g, 56.1 mmol), the mixture was heated under reflux for 16 h and then cooled to room temperature. The mixture was filtered through Celite and then the filtrate was evaporated under reduced pressure. The residue was purified chromatographically (SiO_2; EtOAc/hexanes, 4 : 6) to afford a yellow liquid (2.37 g, 28%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.60–3.71 (m, 12H), 4.60 (s, 4H), 7.43 (d, J = 8.4 Hz, 4H), 7.60 (d, J = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 69.8, 70.3, 70.3, 71.8, 110.8, 118.6, 127.4, 131.8, 143.7; HR-MS (ESI): calcd for $[M + H]^+$ $C_{22}H_{25}N_2O_4^+$, m/z 381.1814; found 381.1836.

Benzonitrile 6. NaH (696 mg, 29.0 mmol) was added to a solution of tetra(ethylene glycol) (2.00 mL, 11.6 mmol) in THF (116 mL) and then the mixture was stirred at room temperature for 30 min. After the addition of 4-cyanobenzylbromide (5.68 g, 29.0 mmol), the mixture was heated under reflux for 16 h and then cooled to room temperature. The mixture was filtered through Celite and then the filtrate was evaporated under reduced pressure. The residue was purified chromatographically (SiO_2; EtOAc/hexanes, 4 : 6) to afford a yellow liquid (4.53 g, 92%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.61–3.69 (m, 16H), 4.59 (s, 4H), 7.43 (d, J = 8.0 Hz, 4H), 7.61 (d, J = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.0, 70.6, 70.6, 70.7, 72.2, 111.2, 118.8, 127.7, 132.2, 143.9; HR-MS (ESI): calcd for $[M + H]^+$ $C_{24}H_{29}N_2O_5^+$, m/z 425.2076; found 425.2099.

Amine 2. $LiAlH_4$ (299 mg, 7.88 mmol) was added to a solution of **5** (1.00 g, 2.63 mmol) in THF (52.6 mL) at 0 °C and then the mixture was heated under reflux for 3 h. After cooling to room temperature, H_2O (2 mL) was added dropwise to quench the reaction; the mixture was dried ($MgSO_4$) and filtered and the filtrate was then concentrated. The residue was purified chromatographically (SiO_2; MeOH/NEt_3/CH_2Cl_2, 5 : 5 : 90). The product isolated was partitioned between $NaOH_{(aq.)}$ (10%, 50 mL) and CH_2Cl_2 (2 × 50 mL); the combined organic phases were dried ($MgSO_4$) and concentrated to afford a yellow liquid (874 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.55–3.60 (m, 4H), 3.60–3.65 (m, 8H), 3.79 (s, 4H), 4.50 (s, 4H), 7.22 (d, J = 8.0 Hz, 4H), 7.26 (d, J = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 45.4, 68.6, 69.9, 72.2, 126.3, 127.2, 136.0, 142.0 (one signal was missing, possibly due to a signal overlap); HR-MS (ESI): calcd for $[M + H]^+$ $C_{22}H_{33}N_2O_4^+$, m/z 389.2440; found 389.2471.

Amine 3. $LiAlH_4$ (268 mg, 7.06 mmol) was added to a solution of **6** (1.00 g, 2.36 mmol) in THF (47.1 mL) at 0 °C and then the mixture was heated under reflux for 3 h. After cooling to room temperature, H_2O (2 mL) was added dropwise to quench the reaction; the mixture was dried ($MgSO_4$) and filtered and the filtrate was then concentrated. The residue was purified chromatographically (SiO_2; MeOH/NEt_3/CH_2Cl_2, 5 : 5 : 90). The product isolated was partitioned between $NaOH_{(aq.)}$ (10%, 50 mL) and CH_2Cl_2 (2 × 50 mL); the combined organic phases were dried ($MgSO_4$) and concentrated to afford a yellow liquid (0.947 g, 93%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.57–3.61 (m, 4H), 3.62–3.66 (m, 12H), 3.83 (s, 4H), 4.52 (s, 4H), 7.25 (d, J = 8.0 Hz, 4H), 7.29 (d, J = 8.0 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.1, 69.2, 70.5, 70.5, 70.5, 72.8, 127.0, 127.9, 136.6, 142.6; HR-MS (ESI): calcd for $[M + H]^+$ $C_{24}H_{37}N_2O_5^+$, m/z 433.2702; found 433.2735.

[2]Catenane 14. A solution of **1** (165 mg, 0.479 mmol), isophthalaldehyde (64.1 mg, 0.478 mmol), and NaTFPB (212 mg, 0.239 mmol) in $CHCl_3$ (23.9 mL) was stirred at 50 °C for 24 h. After cooling to room temperature, the mixture was slowly added to a solution of $NaBH_4$ (726 mg, 19.2 mmol) in MeOH (95.6 mL) and then the organic solvents were evaporated under reduced pressure. The residue was partitioned between H_2O (30 mL) and CH_2Cl_2 (2 × 30 mL); the combined organic phases were dried ($MgSO_4$) and concentrated. The residue was dissolved in DMF (23.9 mL), paraformaldehyde (1.48 g, 47.7 mmol) and formic acid (1.80 mL, 47.7 mmol) were added, and then the solution was stirred at 70 °C for 16 h. The organic solvent was evaporated under reduced pressure and the residue partitioned between $NaOH_{(aq.)}$ (10%, 30 mL) and CH_2Cl_2 (2 × 30 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (NH-silica gel; EtOAc/hexanes, 2 : 8) to afford a colorless oil (132 mg, 58%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.21 (s, 12H), 2.77 (t, J = 5.6 Hz, 8H), 2.86 (t, J = 5.6 Hz, 8H), 3.36 (s, 8H), 3.59 (s, 8H), 3.94 (s, 8H), 6.95 (s, 2H), 6.99 (d, J = 8.0 Hz, 8H), 7.18 (d, J = 8.0 Hz, 8H), 7.23–7.27 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.4, 59.9, 62.3, 68.0, 69.2, 72.3, 126.6, 128.0, 128.6, 128.8, 128.9, 137.2, 137.4, 139.6; HR-MS (ESI): calcd for $[M + H]^+$ $C_{60}H_{77}N_4O_6^+$: m/z 949.5838; found 949.5877.

[2]Catenane 15. A solution of **2** (187 mg, 0.481 mmol), isophthalaldehyde (64.6 mg, 0.482 mmol), and KTFPB (217 mg, 0.240 mmol) in $CHCl_3$ (24.1 mL) was stirred at 50 °C for 24 h. After cooling to room temperature, the mixture was slowly added to a solution of $NaBH_4$ (730 mg, 19.3 mmol) in MeOH (96.4 mL) and then the organic solvents were evaporated under reduced pressure. The residue was partitioned between

H_2O (30 mL) and CH_2Cl_2 (2 × 30 mL); the combined organic phases were dried ($MgSO_4$) and concentrated. The residue was dissolved in DMF (24.1 mL), paraformaldehyde (1.49 g, 48.0 mmol) and formic acid (1.81 mL, 48.0 mmol) were added, and then the solution was stirred at 70 °C for 16 h. The organic solvent was evaporated under reduced pressure and the residue partitioned between $NaOH_{(aq.)}$ (10%, 30 mL) and CH_2Cl_2 (2 × 30 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (NH-silica gel; EtOAc/hexanes, 3 : 7) to afford a colorless oil (119 mg, 48%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.14 (s, 12H), 3.06–3.18 (m, 24H), 3.31 (s, 8H), 3.40 (s, 8H), 4.12 (s, 8H), 6.97 (d, J = 8.0 Hz, 8H), 7.05 (s, 2H), 7.09 (d, J = 8.0 Hz, 8H), 7.21–7.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.5, 60.7, 61.7, 68.7, 69.8, 70.2, 72.7, 126.9, 128.0, 128.5, 128.7, 136.6, 137.8, 139.4 (one signal was missing, possibly due to a signal overlap); HR-MS (ESI): calcd for $[M + H]^+$ $C_{64}H_{85}N_4O_8^+$: m/z 1037.6367; found 1037.6350.

[2]Catenane 16. A solution of **3** (206 mg, 0.476 mmol), isophthalaldehyde (63.8 mg, 0.476 mmol), and RbTFPB (226 mg, 0.238 mmol) in $CHCl_3$ (23.8 mL) was stirred at 50 °C for 24 h. After cooling to room temperature, the mixture was slowly added to a solution of $NaBH_4$ (722 mg, 19.1 mmol) in MeOH (95.3 mL) and then the organic solvents were evaporated under reduced pressure. The residue was partitioned between H_2O (30 mL) and CH_2Cl_2 (2 × 30 mL); the combined organic phases were dried ($MgSO_4$) and concentrated. The residue was dissolved in DMF (23.8 mL), paraformaldehyde (1.48 g, 47.7 mmol) and formic acid (1.80 mL, 47.7 mmol) were added, and then the mixture was stirred at 70 °C for 16 h. The organic solvent was evaporated under reduced pressure and the residue partitioned between $NaOH_{(aq.)}$ (10%, 30 mL) and CH_2Cl_2 (2 × 30 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (NH-silica gel; EtOAc/hexanes, 4 : 6) to afford a colorless oil (80.9 mg, 30%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.08 (s, 12H), 3.21–3.40 (m, 48H), 4.23 (s, 8H), 7.01 (d, J = 8.0 Hz, 8H), 7.06–7.11 (m, 10H), 7.19–7.22 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.5, 61.3, 61.7, 69.1, 70.4, 70.5, 72.9, 127.3, 127.8, 128.1, 128.6, 129.1, 136.7, 138.2, 139.3 (one signal was missing, possibly due to a signal overlap); HR-MS (ESI): calcd for $[M + H]^+$ $C_{68}H_{93}N_4O_{10}^+$: m/z 1125.6892; found 1125.6847.

[2]Catenane 17. A solution of **1** (148 mg, 0.430 mmol), **2** (167 mg, 0.430 mmol), isophthalaldehyde (116 mg, 0.865 mmol), and NaTFPB (382 mg, 0.431 mmol) in $CHCl_3$ (43.0 mL) was stirred at 50 °C for 24 h. After cooling to room temperature, the mixture was slowly added to a solution of $NaBH_4$ (1.30 g, 34.4 mmol) in MeOH (172 mL) and then the organic solvents were evaporated under reduced pressure. The residue was partitioned between H_2O (50 mL) and CH_2Cl_2 (2 × 50 mL); the combined organic phases were dried ($MgSO_4$) and concentrated. The residue was dissolved in DMF (43.0 mL), paraformaldehyde (2.68 g, 86.4 mmol) and formic acid (3.26 mL, 86.4 mmol) were added, and then the solution was stirred at 70 °C for 16 h. The organic solvent was evaporated under reduced pressure and the residue partitioned between $NaOH_{(aq.)}$ (10%, 50 mL) and CH_2Cl_2 (2 × 50 mL). The organic phase was dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (NH-silica gel; EtOAc/hexanes, 3 : 7) to afford **17** (66.8 mg, 16%), **14** (42.8 mg, 21%), and **15** (54.6 mg, 24%), each as a colorless oil; data for **17**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.10 (s, 6H), 2.20 (s, 6H), 2.78 (s, 4H), 2.87–3.00 (m, 8H), 3.11–3.19 (m, 8H), 3.24 (s, 4H), 3.35 (s, 4H), 3.40 (s, 4H), 3.48 (s, 4H), 4.04 (s, 4H), 4.16 (s, 4H), 6.90 (d, J = 8.0 Hz, 4H), 6.95 (s, 1H), 6.97–7.02 (m, 5H), 7.08 (d, J = 8.0 Hz, 4H), 7.13–7.30 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.3, 42.7, 60.0, 60.8, 61.9, 62.0, 68.3, 68.3, 69.3, 69.6, 70.0, 72.7, 72.8, 126.5, 126.9, 127.7, 128.2, 128.2, 128.4, 128.6, 128.7, 128.9, 129.2, 136.4, 137.1, 137.6, 138.2, 139.5 (one signal was missing, possibly due to a signal overlap); HR-MS (ESI): calcd for $[M + H]^+$ $C_{62}H_{81}N_4O_7^+$: m/z 993.6105; found 993.6133.

[2]Catenane 18. A solution of **2** (154 mg, 0.396 mmol), **3** (171 mg, 0.395 mmol), isophthalaldehyde (106 mg, 0.790 mmol), and RbTFPB (376 mg, 0.396 mmol) in $CHCl_3$ (39.6 mL) was stirred at 50 °C for 24 h. After cooling to room temperature, the mixture was slowly added to a solution of $NaBH_4$ (1.20 g, 31.7 mmol) in MeOH (158 mL) and then the organic solvents were evaporated under reduced pressure. The residue was partitioned between H_2O (40 mL) and CH_2Cl_2 (2 × 40 mL); the combined organic phases were dried ($MgSO_4$) and concentrated. The residue was dissolved in DMF (39.6 mL), paraformaldehyde (2.46 g, 79.3 mmol) and formic acid (2.99 mL, 79.3 mmol) were added, and then the mixture was stirred at 70 °C for 16 h. The organic solvent was evaporated under reduced pressure and the residue partitioned between $NaOH_{(aq.)}$ (10%, 40 mL) and CH_2Cl_2 (2 × 40 mL). The organic phase was dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (NH-silica gel; EtOAc/hexanes, 3 : 7) to afford **18** (68.7 mg, 16%), **15** (53.5 mg, 26%), and **16** (36.7 mg, 16%), each as a colorless oil; data for **18**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.08 (s, 6H), 2.12 (s, 6H), 3.14–3.41 (m, 44H), 4.18 (s, 4H), 4.20 (s, 4H), 6.96–7.04 (m, 9H), 7.07 (d, J = 8.0 Hz, 4H), 7.11 (d, J = 8.0 Hz, 4H), 7.15 (s, 1H), 7.17–7.20 (m, 3H), 7.22–7.26 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.5, 42.5, 60.8, 61.4, 61.7, 61.8, 68.9, 69.0, 70.2, 70.2, 70.3, 70.5, 72.8, 73.0, 126.9, 127.3, 127.8, 128.0, 128.1, 128.6, 128.7, 128.9, 129.1, 136.5, 136.8, 138.0, 138.1, 139.4, 139.5 (two signals were missing, possibly due to signal overlap); HR-MS (ESI): calcd for $[M + Na]^+$ $C_{66}H_{88}N_4O_9Na^+$: m/z 1103.6449; found 1103.6437.

[2]Catenane 19. A solution of **1** (156 mg, 0.453 mmol), **3** (195 mg, 0.451 mmol), isophthalaldehyde (121 mg, 0.902 mmol), and NaTFPB (400 mg, 0.451 mmol) in $CHCl_3$ (75.1 mL) was stirred at 50 °C for 24 h. After cooling to room temperature, the mixture was slowly added to a solution of $NaBH_4$ (1.06 g, 28.0 mmol) in MeOH (140 mL) and then the organic solvents were evaporated under reduced pressure. The residue was partitioned between H_2O (50 mL) and CH_2Cl_2 (2 × 50 mL); the combined organic phases were dried ($MgSO_4$) and concentrated. The residue was dissolved in DMF (45.1 mL), paraformaldehyde (2.80 g, 90.2 mmol) and formic acid (3.41 mL, 90.4 mmol) were added, and then the solution was

stirred at 70 °C for 16 h. The organic solvent was evaporated under reduced pressure and the residue partitioned between $NaOH_{(aq.)}$ (10%, 50 mL) and CH_2Cl_2 (2 × 50 mL). The organic phase was dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (NH-silica gel; EtOAc/hexanes, 3 : 7) to afford **19** (27.3 mg, 6%), **14** (41.1 mg, 19%), and **16** (3.6 mg, 1%), each as a colorless oil; data for **19**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.05 (s, 6H), 2.16 (s, 6H), 2.92–3.02 (m, 8H), 3.07–3.15 (m, 8H), 3.19 (s, 4H), 3.26–3.34 (m, 8H), 3.36 (s, 4H), 3.39 (s, 4H), 3.44 (s, 4H), 4.17 (s, 4H), 4.23 (s, 4H), 6.92 (s, 1H), 6.98 (d, J = 8.0 Hz, 4H), 7.02 (d, J = 8.0 Hz, 4H), 7.07–7.15 (m, 7H), 7.17 (s, 1H), 7.20 (d, J = 8.0 Hz, 4H), 7.23–7.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.3, 42.6, 60.0, 61.4, 61.7, 62.0, 68.5, 68.8, 69.8, 69.8, 70.3, 72.7, 73.1, 126.6, 127.3, 127.7, 127.9, 128.1, 128.4, 128.6, 129.0, 129.1, 129.4, 136.3, 137.2, 137.6, 138.3, 139.3 (two signals were missing, possibly due to signal overlap); HR-MS (ESI): calcd for $[M + H]^+$ $C_{64}H_{85}N_4O_8^+$: m/z 1037.6367; found 1037.6322.

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Notes and references

1 For recent reviews, see: (*a*) M. E. Belowich and J. F. Stoddart, *Chem. Soc. Rev.*, 2012, **41**, 2003; (*b*) J.-C. Chambron and J.-P. Sauvage, *New J. Chem.*, 2013, **37**, 49; (*c*) S. P. Black, J. K. M. Sanders and A. R. Stefankiewicz, *Chem. Soc. Rev.*, 2014, **43**, 1861; (*d*) V. Marti-Centelles, M. D. Pandey, M. I. Burguete and S. V. Luis, *Chem. Rev.*, 2015, **115**, 8736.

2 (*a*) M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, 1964, **86**, 213; (*b*) N. F. Curtis, *Coord. Chem. Rev.*, 1968, **3**, 3; (*c*) O. Costisor and W. Linert, *Metal Mediated Template Synthesis of Ligands*, World Scientific Publishing, Singapore, 2004.

3 For reviews, see: (*a*) B. Champin, P. Mobian and J.-P. Sauvage, *Chem. Soc. Rev.*, 2007, **36**, 358; (*b*) J. E. Beves, B. A. Blight, C. J. Campbell, D. A. Leigh and R. T. McBurney, *Angew. Chem., Int. Ed.*, 2011, **50**, 9260.

4 (*a*) M. Meyer, A.-M. Albrecht-Gary, C. O. Dietrich-Buchecker and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1997, **119**, 4599; (*b*) J. Brueggemann, S. Bitter, S. Mueller, W. M. Mueller, U. Mueller, N. M. Maier, W. Lindner and F. Voegtle, *Angew. Chem., Int. Ed.*, 2006, **46**, 254; (*c*) J. Guo, P. C. Mayers, G. A. Breault and C. A. Hunter, *Nat. Chem.*, 2010, **2**, 218; (*d*) J.-P. Sauvage and D. B. Amabilino, *Top. Curr. Chem.*, 2012, **323**, 107.

5 (*a*) K. S. Chichak, S. J. Cantrill, A. R. Pease, S.-H. Chiu, G. W. V. Cave, J. L. Atwood and J. F. Stoddart, *Science*, 2004, **304**, 1308; (*b*) S.-L. Huang, Y.-J. Lin, Z.-H. Li and G.-X. Jin, *Angew. Chem., Int. Ed.*, 2014, **53**, 11218; (*c*) F. L. Thorp-Greenwood, A. N. Kulak and M. J. Hardie, *Nat. Chem.*, 2015, **7**, 526.

6 D. A. Leigh, R. G. Pritchard and A. J. Stephens, *Nat. Chem.*, 2014, **6**, 978.

7 (*a*) G. W. Gokel, *Crown Ethers and Cryptands*, The Royal Society of Chemistry, Cambridge, 1991; (*b*) *Crown Ethers and Analogous Compounds*, ed. M. Hiraoka, Elsevier, Amsterdam, 1992; (*c*) M. C. T. Fyfe and J. F. Stoddart, in *Advances in Supramolecular Chemistry*, ed. G. W. Gokel, JAI, London, 1999, vol. 5, pp. 1–53.

8 (*a*) G. Kaiser, T. Jarrosson, S. Otto, Y.-F. Ng, A. D. Bond and J. K. M. Sanders, *Angew. Chem., Int. Ed.*, 2004, **43**, 1959; (*b*) S. A. Vignon, T. Jarrosson, T. Iijima, H.-R. Tseng, J. K. M. Sanders and J. F. Stoddart, *J. Am. Chem. Soc.*, 2004, **126**, 9884; (*c*) Y.-H. Lin, C.-C. Lai, Y.-H. Liu, S.-M. Peng and S.-H. Chiu, *Angew. Chem., Int. Ed.*, 2013, **52**, 10231; (*d*) K.-D. Wu, Y.-H. Lin, C.-C. Lai and S.-H. Chiu, *Org. Lett.*, 2014, **16**, 1068; (*e*) T.-H. Ho, C.-C. Lai, Y.-H. Liu, S.-M. Peng and S.-H. Chiu, *Chem. – Eur. J.*, 2014, **20**, 4563; (*f*) Y.-H. Lin, C.-C. Lai and S.-H. Chiu, *Org. Biomol. Chem.*, 2014, **12**, 2907; (*g*) Y.-W. Wu, P.-N. Chen, C.-F. Chang, C.-C. Lai and S.-H. Chiu, *Org. Lett.*, 2015, **17**, 2158; (*h*) Y.-W. Wu, S.-T. Tung, C.-C. Lai, Y.-H. Liu, S.-M. Peng and S.-H. Chiu, *Angew. Chem., Int. Ed.*, 2015, **54**, 11745.

9 S.-T. Tung, C.-C. Lai, Y.-H. Liu, S.-M. Peng and S.-H. Chiu, *Angew. Chem., Int. Ed.*, 2013, **52**, 13269.

10 For chemosensors that can differentiate between Na^+ and K^+ ions, see: (*a*) A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson and M. Nieuwenhuizen, *Chem. Commun.*, 1996, 1967; (*b*) T. Jin, *Chem. Commun.*, 1999, 2491; (*c*) F. He, Y. Tang, S. Wang, Y. Li and D. Zhu, *J. Am. Chem. Soc.*, 2005, **127**, 12343; (*d*) M. Barush, W. Qin, R. A. L. Vallée, D. Beljonne, T. Rohand, W. Dehaen and N. Boens, *Org. Lett.*, 2005, **7**, 4377; (*e*) S.-Y. Hsueh, C.-C. Lai, Y.-H. Liu, S.-M. Peng and S.-H. Chiu, *Angew. Chem., Int. Ed.*, 2007, **46**, 2013; (*f*) X. Wang, J. Zhu and D. B. Smithrud, *J. Org. Chem.*, 2010, **75**, 3358; (*g*) X. Zhou, F. Su, Y. Tian, C. Youngbull, R. H. Johnson and D. R. Meldrum, *J. Am. Chem. Soc.*, 2011, **133**, 18530; (*h*) X. Kong, F. Su, L. Zhang, J. Yaron, F. Lee, Z. Shi, Y. Tian and D. R. Meldrum, *Angew. Chem., Int. Ed.*, 2015, **54**, 12053.

11 We methylated the [2]catenanes to avoid their slow decomposition in $CDCl_3$; similar tertiary amino derivatives have been found to be much more robust (ref. 8*h*). For other examples of this methylation method, see: (*a*) K. Nakazono, S. Kuwata and T. Takata, *Tetrahedron Lett.*, 2008, **49**, 2397; (*b*) S. Suzuki, K. Nakazono and T. Takata, *Org. Lett.*, 2010, **12**, 712; (*c*) T.-W. Lu, C.-F. Chang, C.-C. Lai and S.-H. Chiu, *Org. Lett.*, 2013, **15**, 5742.

