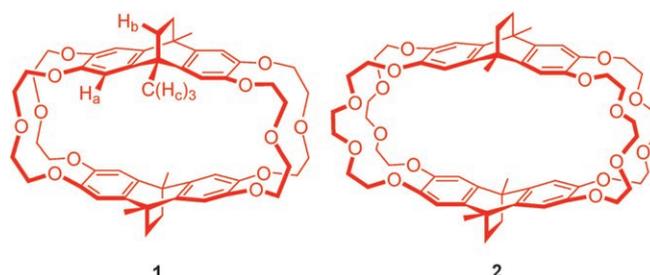


Highly Selective Na⁺-Templated Formation of [2]Pseudorotaxanes Exhibiting Significant Optical Outputs**

Sheng-Yao Hsueh, Chien-Chen Lai, Yi-Hung Liu, Shie-Ming Peng, and Sheng-Hsien Chiu*

The diverse range of binding geometries exhibited by metal ions and their relatively stable interactions with ligands can be exploited for the efficient template-directed synthesis of macrocycles,^[1] supramolecular architectures,^[2] and interlocked molecules.^[3] Although the formation of rotaxanes or pseudorotaxanes has been demonstrated using transition-metal ions coordinated to four (tetrahedral and square planar),^[4] five (trigonal bipyramidal and square pyramidal),^[5] and six (octahedral)^[6] donor atoms, alkali-metal ions, which are useful templates for the synthesis of crown ethers,^[7] are rarely used to direct the construction of such complexes. In one example, Li⁺ ions have been used to assist the formation of a unique donor–acceptor pseudorotaxane,^[8] but it appears that Na⁺ ions play a similar role in that system.^[9] We became interested in forming pseudorotaxanes in solution with high efficiency and selectivity toward a single species of alkali-metal ion—especially if we could differentiate between the physiologically important,^[10] but chemically similar, Na⁺ and K⁺ ions.^[11] Herein, we report a new molecular recognition system based on the molecular cage **1** (Scheme 1) and two different threadlike molecules (anthraquinone and squaraine), each of which forms a pseudorotaxane complex with **1** in the presence of templating Na⁺ ions and exhibits high selectivity over the other alkali-metal ions tested. This ion-specific templating effect was easy to monitor because the complexation and decomplexation of the pseudorotaxane complexes in solution occurred with color changes that were detectable to the naked eye. It appears from the solid-state structures that the dramatic Na⁺/K⁺ selectivity in this supramolecular system results from the different positions and ligand complexation geometries of the metal ions bound by the crown ether motifs of the molecular cage.



Scheme 1. Molecular cages **1** and **2**.

Previously, we demonstrated that molecular cage **2** and anthraquinone (**3**, Scheme 2) can form pseudorotaxane-like complexes in solution when K⁺ ions are present.^[12] We suspected that greater ion-selective templating behavior would arise if we replaced the two openings resembling dibenzo[24]crown-8 (DB24C8) in **2** with two relatively smaller and more rigid units resembling dibenzo[18]crown-6 (DB18C6, Scheme 2). Thus, we synthesized the corresponding molecular cage **1** in three steps from 2,3,6,7-tetrahydroxy-9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene (see the Supporting Information).

The ¹H NMR spectrum (Figure 1B) of a mixture of macrocycle **1**, anthraquinone, and NaClO₄ (2:2:4 mM) in CDCl₃/CD₃CN (1:1) exhibits three sets of resonances: 1) those of the Na⁺-complexed molecular cage **1** (Figure 1A), 2) the free anthraquinone (Figure 1C), and 3) the complex formed between **1**, anthraquinone, and Na⁺ ions. This finding implies that the rates of complexation and decomplexation are both slow on the ¹H NMR spectroscopic timescale at 400 MHz and 298 K. The upfield shifts of the signals of the aromatic protons of both components imply that stacking of their aromatic rings occurs within the supramolecular complex. By using a single-point method,^[13] we determined the association constant (*K*_a) of this system to be 660 M⁻¹ in CDCl₃/CD₃CN (1:1). In contrast, the ¹H NMR spectrum of a mixture of macrocycle **1**, anthraquinone, and KPF₆ (2:2:4 mM) in CDCl₃/CD₃CN (1:1) exhibits negligible shifts of the anthraquinone signals relative to those of the uncomplexed molecule, which suggests that K⁺ ions are very poor templates for the formation of the corresponding pseudorotaxane complex (Figure 1D).

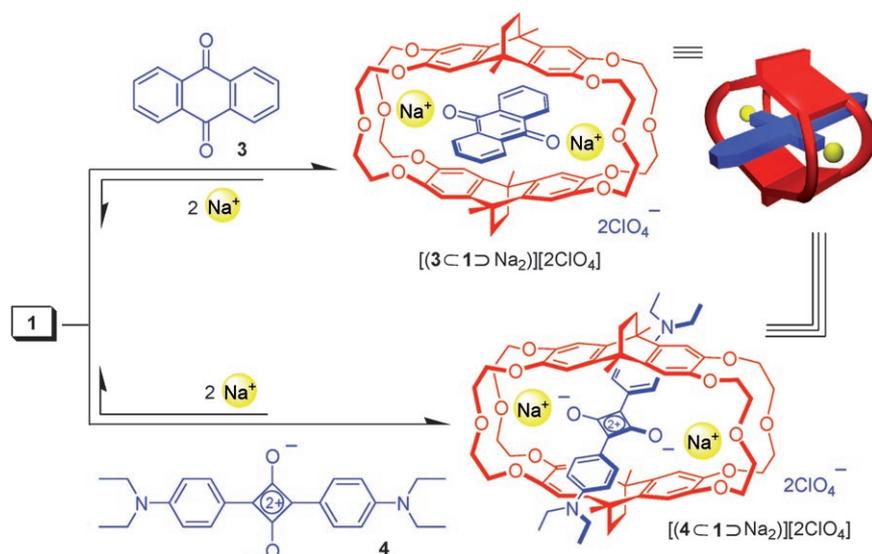
We grew single crystals suitable for X-ray crystallography by liquid diffusion of diisopropyl ether into a solution of molecular cage **1**, NaClO₄, and anthraquinone (1:2:1) in CH₃CN. The solid-state structure (Figure 2) reveals the expected [2]pseudorotaxane binding geometry of the complex [3C**1**⊃Na₂]²⁺,^[14,15] the rodlike anthraquinone unit penetrates through the two 28-membered rings while its two

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[**] This study was supported by the National Science Council, Taiwan (NSC-95-2113M-002-016-MY3 and NSC-95-2752M-002-002-PAE).

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Scheme 2. Complexation of molecular cage **1** with threadlike guests **3** and **4** in the presence of templating Na^+ ions.

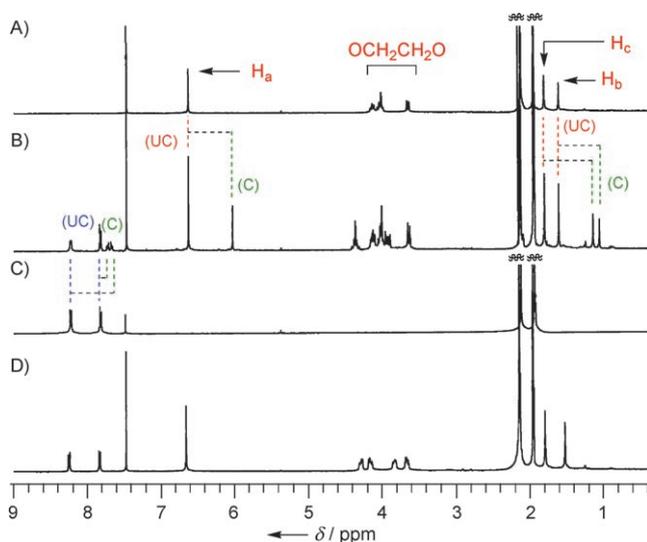


Figure 1. Partial ^1H NMR spectra (400 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1:1), 298 K) of A) a mixture of **1** (2 mM) and NaClO_4 (4 mM), B) a mixture of **1** (2 mM), **3** (2 mM), and NaClO_4 (4 mM), C) **3**, and D) a mixture of **1** (2 mM), **3** (2 mM), and KClO_4 (4 mM). The descriptors (C) and (UC) refer to the signals of the complexed and uncomplexed states of the components, respectively.

oxygen atoms coordinate to the two Na^+ ions, which are themselves bound within the [18]crown-6 units of the molecular cage.

The solution of **1**, **3**, and NaClO_4 (4:4:8 mM) in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1:1) displayed a clearly observable orange color, possibly as a result of charge-transfer interactions between the molecular cage and the anthraquinone in the pseudorotaxane-like complex (Figure 3). The addition of Li^+ , K^+ , or Cs^+ ions at the same concentration did not cause a noticeable color change of the molecular cage/anthraquinone solution, thus suggesting that Na^+ ions templated the formation of the pseudorotaxane-like complex quite selectively among these

common alkali-metal ions. As the absorption arising from charge-transfer interactions between the electron-rich phenol units of the molecular cage and the electron-deficient anthraquinone was not very striking to the naked eye, we turned our attention toward complexes formed using the rodlike squaraine (**4**, Scheme 2), which is an important near-IR dye with potential applications in many areas, such as nonlinear optics, photovoltaics, biological labeling, and photodynamic therapy.^[16]

The ^1H NMR spectrum of a solution of macrocycle **1**, squaraine, and NaClO_4 (2:2:4 mM) in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1:1) exhibits proton shifts that are similar to those of the $[\mathbf{3C1DNa}_2][\mathbf{2ClO}_4]$ system, which suggests that the geometry of the complex $[\mathbf{4C1DNa}_2][\mathbf{2ClO}_4]$ is likely to

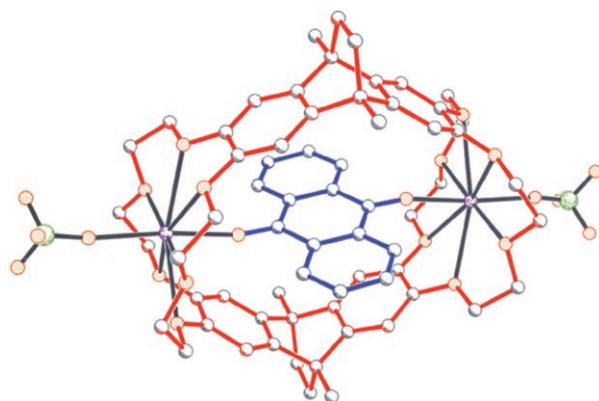


Figure 2. Ball-and-stick representation of the solid-state structure of $[\mathbf{3C1DNa}_2][\mathbf{2ClO}_4]$. Atom labels: C, gray; O, orange; Na, purple; Cl, green.

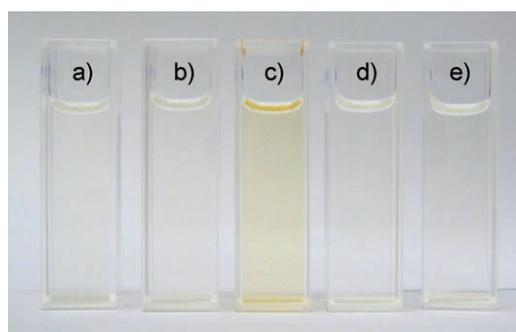


Figure 3. Photograph of vials containing solutions of **1** and anthraquinone (4 mM each) in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1:1) in the a) absence and b)–e) in the presence of b) Li^+ , c) Na^+ , d) K^+ , and e) Cs^+ ions (8 mM each).

be that of a pseudorotaxane (see the Supporting Information). The Na^+ ions templated the formation of the complex $[\mathbf{4C1DNa}_2][\mathbf{2ClO}_4]$ much more efficiently than they did the

corresponding anthraquinone complex; the binding constant (K_a) between the Na-complexed molecular cage **1** and squaraine in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (1:1) was 9600M^{-1} ,^[13] which is more than tenfold higher than that of the anthraquinone complex. The stronger binding affinity of squaraine to the Na-complexed molecular cage **1**, relative to that of anthraquinone, may be the result of greater steric compatibility and/or the greater electron densities of the oxygen atoms of **4**.

We obtained single crystals of the complex suitable for X-ray crystallography by liquid diffusion of diisopropyl ether into a solution of molecular cage **1**, NaBF_4 , and squaraine (1:2:1) in CH_3CN . The solid-state structure (Figure 4) confirms the expected [2]pseudorotaxane binding geometry of the complex $[\mathbf{4}\mathbf{C}\mathbf{1}\mathbf{D}\mathbf{Na}_2]^{2+}$,^[17] in which the rodlike squaraine unit penetrates through the two 28-membered rings, while its two oxygen atoms coordinate to the two Na^+ ions, which are themselves complexed to the two [18]crown-6 units of **1**.

Figure 5 illustrates that, among all of the alkali-metal ions tested, the blue color of the solution of **1** and squaraine turned red only in the presence of Na^+ ions. The quantum yield of squaraine dye at a wavelength of approximately 650 nm

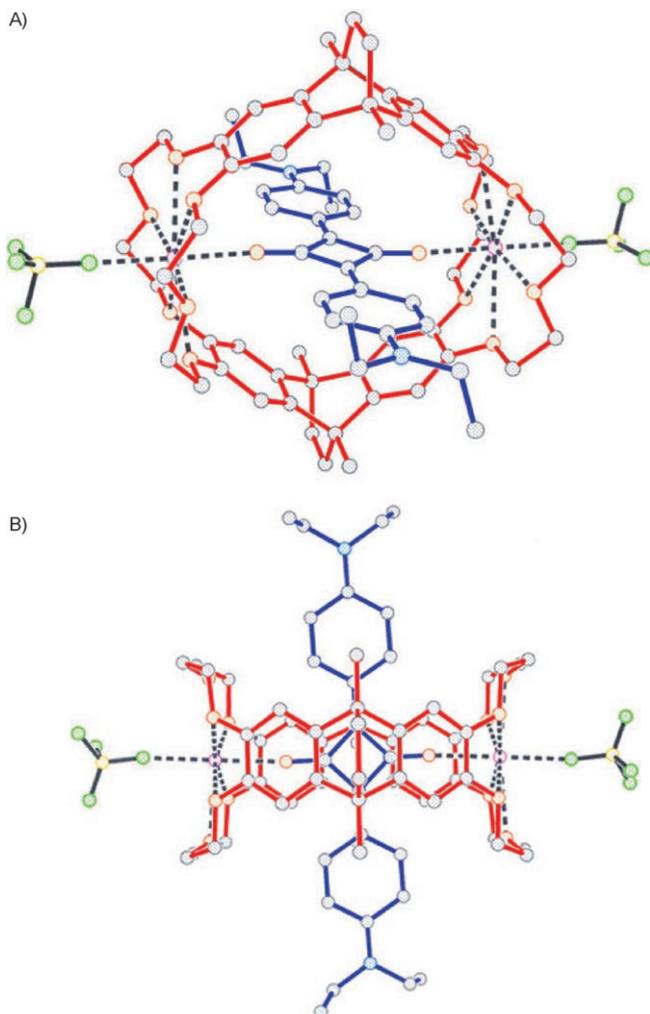


Figure 4. Ball-and-stick representations of the solid-state structure $[\mathbf{4}\mathbf{C}\mathbf{1}\mathbf{D}\mathbf{Na}_2][\mathbf{2}\mathbf{BF}_4]$. Atom labels: C, gray; O, orange; N, blue; Na, purple; B, yellow; F, green.

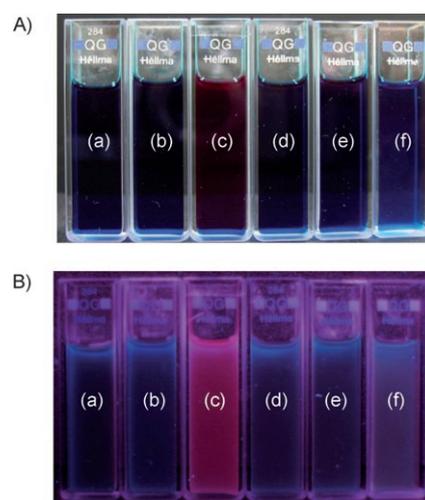


Figure 5. Photographs of the A) visible and B) fluorescence (excitation at 354 nm) behavior of mixtures of **1** and **4** (2 mM each) in $\text{CHCl}_3/\text{CH}_3\text{CN}$ (1:1) in the a) absence and b)–f) presence of 2 equiv of b) Li^+ , c) Na^+ , d) K^+ , and e) Cs^+ and f) 2 equiv of Na^+ and 20 equiv of K^+ ions.

decreases significantly in polar solvents.^[18] Thus, the color of a squaraine solution is related to the polarity of the solvent system; for example, CHCl_3 solutions of squaraine and its mixture with molecular cage **1** displayed similar red-to-blue color changes when the more-polar CH_3CN was added (see the Supporting Information). This finding suggests that the red color of the $\text{CHCl}_3/\text{CH}_3\text{CN}$ (1:1) solution of molecular cage **1**, squaraine, and Na^+ ions results from the formation of the corresponding pseudorotaxane-like complex in solution; that is, the relatively nonpolar molecular cage protects the squaraine dye from solvation by polar CH_3CN molecules.

Figure 6 provides a comparison of the emission spectra observed after adding Na^+ and K^+ ions (2 equiv), respectively, to an equimolar ($1.3 \times 10^{-4}\text{M}$) solution of molecular cage **1** and squaraine **4**; it is clear that the presence of Na^+ ions enhanced the fluorescence of squaraine substantially. Interestingly, the addition of 20 equivalents of K^+ ions to the red solution of $[\mathbf{4}\mathbf{C}\mathbf{1}\mathbf{D}\mathbf{Na}_2][\mathbf{2}\mathbf{ClO}_4]$ led to a substantial degree of

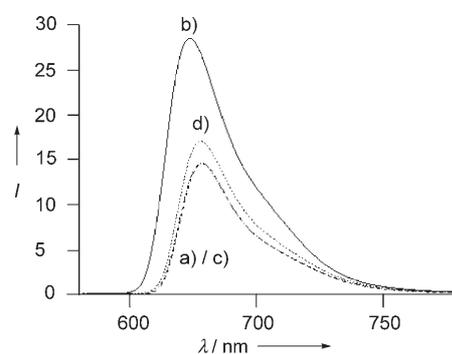


Figure 6. Fluorescence spectra ($\text{CDCl}_3/\text{CD}_3\text{CN}$ (1:1), 298 K; excitation at 400 nm) of a) an equimolar mixture ($1.3 \times 10^{-4}\text{M}$) of **1** and **4**, b) the system in (a) after the addition of 2 equiv of NaClO_4 , c) the system in (a) after the addition of 2 equiv of KPF_6 , and d) the system in (b) after the addition of 20 equiv of KPF_6 .

dissociation of the pseudorotaxane complex: the color of the solution turned immediately from red to blue (compare vials f in Figure 5A,B). This result suggests that while K^+ ions can compete with Na^+ ions for complexation to **1** in solution, the K^+ -complexed molecular cage displays a much weaker binding affinity to the squaraine thread.

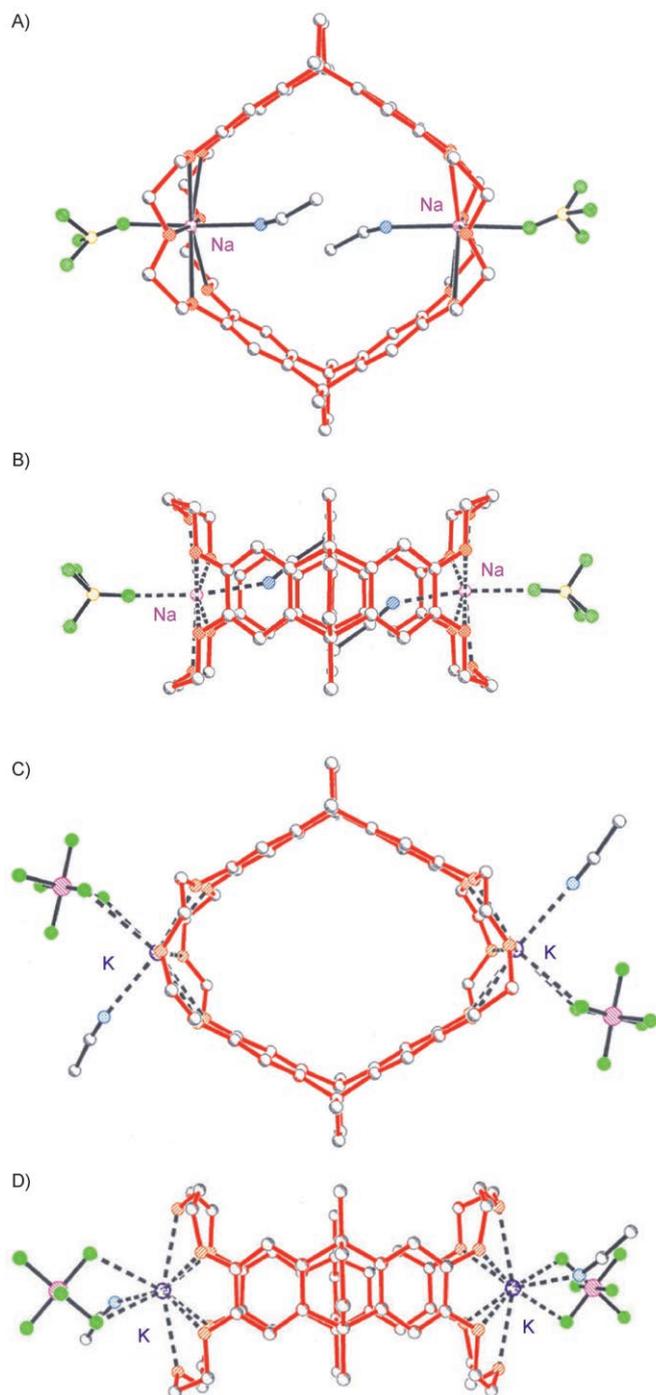


Figure 7. Ball-and-stick representations of the solid-state structures of $[(1\text{Na}_2)\cdot 2\text{MeCN}][2\text{BF}_4]$: a) side view; b) top view, and $[(1\text{K}_2)\cdot 2\text{MeCN}][2\text{PF}_6]$: c) side view; d) top view. Atom labels: C, gray; O, orange; N, blue; Na, light purple; B, yellow; P, pink; K, purple; F, green.

Our finding that the metal-templating motifs in anthraquinone and squaraine (that is, the aromatic rings with two carbonyl groups) both highly favor Na^+ over K^+ ions in templating the formation of their respective [2]pseudorotaxanes seems puzzling, as they are of different sizes. To determine how the molecular cage **1** coordinates to these two metal ions we grew single crystals suitable for X-ray crystallography by liquid diffusion of diisopropyl ether into solutions of molecular cage **1** and NaBF_4 or KPF_6 (1:2 molar ratio) in CH_3CN . The solid-state structures reveal that each Na^+ (Figure 7A,B) and K^+ (Figure 7C,D) ion is bound to all six oxygen atoms of the individual crown ether units of molecular cage **1**.^[19,20] The [18]crown-6-complexed Na^+ ions are also coordinated by labile CH_3CN ligands located within the cavity of molecular cage **1**; clearly these ligands could be replaced by bidentate ligands such as anthraquinone and squaraine. In contrast, the crown ether motifs of the molecular cage **1** position their K^+ ions outward from the internal cavity, thereby leaving no internal coordination sites for templating bidentate ligands. Thus, it seems that differences in the coordination geometries and ligand binding sites of the complexed metal ions are responsible for molecular cage **1** forming [2]pseudorotaxane structures in the presence of Na^+ ions, but not K^+ ions, even when the bidentate ligands have different sizes.

We have demonstrated that Na^+ ions behave as highly selective templates, relative to K^+ and other alkali-metal ions, for the formation of pseudorotaxanes from the molecular cage **1** and two threadlike molecules (anthraquinone and squaraine) in $\text{CD}_3\text{CN}/\text{CDCl}_3$ (1:1). In addition to this ion-specific binding, the complexation and decomplexation of the pseudorotaxane-like complexes in solution is observable by the naked eye. We believe that rotaxanes constructed from **1** and squaraine derivatives will protect this sensitive dye from decay,^[16f,g] furthermore, they have potential for application as chemosensors and molecular switches that exhibit significant optical outputs. Such systems are currently under investigation.

Received: October 11, 2006

Published online: February 7, 2007

Keywords: alkali metals · host–guest systems · molecular cages · pseudorotaxanes · templating effect

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