## ORIGINAL ARTICLE

# Formation of a pseudorotaxane, capable of sensing cations via dethreading molecular motion, from a cryptand and bipyridinium salts

Masahiro Muraoka · Mamoru Ohta · Yuko Mizutani · Mashio Takezawa · Ayuri Matsumoto · Yohji Nakatsuji

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Abstract A new type of cryptand-based pseudorotaxane was prepared, utilizing a novel cryptand incorporating two aromatic rings as a wheel component, combined with various bipyridinium salts as the axle component. These pseudorotaxanes exhibited charge-transfer absorption at approximately 380 nm due to  $\pi$ -electron interactions between the cryptand and the bipyridinium salt. Upon addition of one equivalent of sodium ion to the pseudorotaxane, this absorption was observed to disappear as a result of displacement of the bipyridinium salt by the sodium.

**Keywords** Pseudorotaxanes · Cryptands · Bipyridinium salts · Charge-transfer interaction · Threading–dethreading molecular motion

### Introduction

To date, substantial effort has been devoted to the development of chemosensors for both ionic and neutral species [1-3]. In the case of chemosensors utilizing molecular recognition, it is particularly important that such systems are capable of responding to analytes with a high degree of both selectivity and sensitivity. In order to achieve this

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Department of Applied Chemistry, Faculty of Engineering, Osaka Institute of Technology, Ohmiya, Asahi-ku,

Osaka 535-8585, Japan

goal, researchers have pursued the development of chemosensors based on highly efficient host molecules (or receptors), including crown ether derivatives.

Recently, various interlocked molecules, such as rotaxanes and catenanes, have been investigated as both chemosensors [4–14] and molecular machines [15–18]. These interlocked molecules can bind specific guest molecules, including alkali metal cations [7-10] and chloride and sulfate anions [11-14], inside three-dimensional cavities. In addition, molecular recognition can be achieved by utilizing pseudorotaxanes [19–22] to sense analytes via a displacement type of molecular motion [23–25]. For example, Stoddart and coworkers [20, 21] reported that [2]pseudorotaxanes can be used to obtain an optical response upon alkali metal binding, based on the unthreading of the axle component from the wheel component. Beer and coworkers [22] reported that sulfate anion complexation by an isophthalamide macrocycle in a [2]pseudorotaxane resulted in displacement of a threaded molecule, with a subsequent loss of color. Both of the above preliminary results required a substantial excess of the triggering species in order to achieve displacement of the thread. This suggests that such displacement may be optimized when the non-covalent wheel-axle interaction is relatively weak in the pseudorotaxane while the complexation ability of the wheel component toward the trigger (or analyte) is proportionately strong. Cryptands are promising candidates for the formation of rotaxanes in conjunction with various threads [26-43]. Because cryptands have in the past been employed to achieve strong binding of metal cations and organic molecules within a three-dimensional cavity [44-46], the displacement-type molecular motion of rotaxanes composed of a bipyridinium salt as the axle component and a cryptand as the wheel component can be expected to occur upon addition of metal cations. Gibson and Huang et al. have performed pioneering work in this area and reported that pseudorotaxanes formed

M. Muraoka ( $\boxtimes$ ) · M. Ohta · Y. Mizutani · M. Takezawa · A. Matsumoto · Y. Nakatsuji

e-mail: muraoka@chem.oit.ac.jp; nakatsuji@chem.oit.ac.jp

Herein, we describe a highly sensitive alkali metal cation-switchable pseudorotaxane, newly designed and synthesized by our research group, formed from the inclusion complex of a bipyridinium salt with a cryptand. The threading–dethreading molecular motion of this pseudorotaxane has been characterized by studies of the binding between the cryptand and bipyridinium salt based on UV– Vis and <sup>1</sup>H NMR spectral changes.

## **Results and discussion**

#### Synthesis

Based on work with monoazacryptands as alkali metal cation carriers for liquid membrane transport, reported previously by our group [51–53], the new cryptand **1** was designed. The intent was to obtain a molecule containing two  $\pi$ -electron-rich aromatic rings in order to stabilize the  $\pi$ -electron-poor aromatic rings of bipyridinium salts through  $\pi$ – $\pi$  stacking (Scheme 1). Cryptand **1** was prepared via the intermolecular [1+1] macrocyclization reaction of *cis*-2,9-bis(bromomethyl)-2,9-dimethyl-15-crown-5 [54] with a diol [55] under basic conditions [56] as summarized in Scheme 2, resulting in a 33 % yield. The structure of **1** was ascertained by <sup>1</sup>H NMR, <sup>13</sup>C NMR, mass spectrometry and elemental analysis.

#### Pseudorotaxane formation

Initial evidence of pseudorotaxane formation based on a combination of cryptand 1 with bipyridinium salts was provided by UV–Vis spectroscopy as shown in Fig. 1. When the colorless cryptand 1 solution (Fig. 1a) was mixed with a colorless solution of dimethyl bipyridinium



Scheme 2 Synthesis of macrocycle 1. Reagents and conditions: *i* tri(ethylene glycol) ditosylate,  $K_2CO_3$ ,  $CH_3CN$ , reflux, 68 h, 69 %; *ii cis*-2,9-bis(bromomethyl)-2.9-dimethyl-15-crown-5, NaH, di(ethylene glycol) dimethyl ether, 120 °C, 79 h, 33 %

salt 2 in acetone (Fig. 1c), a pale yellow coloration was observed as a result of charge-transfer absorption at approximately 380 nm, as evident in the UV–Vis spectrum shown in Fig. 1b. This absorption can be attributed to  $\pi$ -stacking between the bipyridinium and phenylene rings.

Further evidence of the pseudorotaxane structure was provided by changes in <sup>1</sup>H NMR spectra. The binding behavior of the cryptand with bipyridinium salts was examined via the addition of one molar equivalent of the salt to a solution of the cryptand in acetone- $d_6$ . The <sup>1</sup>H NMR spectra of cryptand 1, dimethyl bipyridinium salt 2, and an equimolar mixture of 1 and 2 (1  $\supset$  2) in acetone- $d_6$ are shown in Fig. 2. Upon addition of dimethyl bipyridinium salt 2, slight upfield shifts are observed in the signals of the phenylene protons (d and e) of cryptand 1, implying  $\pi$ - $\pi$  interactions between the electron-rich benzene rings of the macrocycle and the positively charged bipyridinium salt. Thus, it appears that cryptand 1 forms a stable complex with dimethyl bipyridinium salt 2 through  $\pi$ - $\pi$  interactions, indicating the formation of a [2]pseudorotaxane.



Scheme 1 Schematic representation of formation of a pseudorotaxane and dethreading molecular motion



Fig. 1 *Top*: Photographs depicting the color change (acetone, 10 mM); *bottom*: partial UV–Vis spectra (acetone, 10 mM) of **a** 1, **b** an equimolar mixture of 1 and 2, and **c** 2



**Fig. 2** Partial <sup>1</sup>H NMR spectra (300 MHz, acetone- $d_6$ , 293 K) of **a 1**, **b** an equimolar mixture (15 mM) of **1** and **2**, and **c 2** 

The job plot [57] presented in Fig. 3, based on <sup>1</sup>H NMR spectroscopic data measured in acetone- $d_6$ , demonstrates that the stoichiometry in solution of the complex  $1 \supset 2$  was 1:1. The binding properties of cryptand 1 were estimated by quantitative <sup>1</sup>H NMR titration experiments in acetone- $d_6$  in which cryptand 1 was combined with dimethyl bipyridinium salt 2 as well as bipyridinium salt derivatives 3 and 4, as shown in Fig. 4. During these titrations, the <sup>1</sup>H NMR shift changes of the phenylene



Fig. 3 Job plot showing the 1:1 stoichiometry of the complex between 1 and 2 in acetone- $d_6$ : [1] + [2] = 5.0 mM;  $\Delta \delta$  = chemical shift change for proton d of 1



Fig. 4 Structure of the macrocycle 1 and the axles 2-4 for the [2]pseudorotaxanes

protons of the macrocycle (d) were monitored [58]. Measuring the upfield shifts of these protons upon the addition of bipyridinium salts 2–4 allowed the association constants  $(K_a)$  for the complexations to be determined. The association constants thus derived for each complexation are presented in Table 1. The association constants for the complexation of cryptand 1 with all three bipyridinium salts proved to be all on the same order of magnitude.

**Table 1** Association constants  $(K_a)$  [M<sup>-1</sup>] for complexes of macrocycle **1** with bipyridinium salt derivatives **2**, **3** and **4** as determined by <sup>1</sup>H NMR titrations in acetone- $d_6$  at 293 K

Guest	$K_{\rm a}  ({ m M}^{-1})$	$\Delta_0 \text{ (ppm)}$
2	$1.8 \times 10^{2}$	0.41
3	$1.3 \times 10^{2}$	0.41
4	$2.1 \times 10^{2}$	0.57

Error < 8 %. Determined by chemical shift changes of macrocycle **1** proton d during titration experiments followed by non-linear least-squares data treatment as reported by Hirose [58]. An initial host concentration of 2.0 mM was used for the titrations

NOE experiments provided useful information and further evidence of the pseudorotaxane formation, in which bipyridinium salt 2 threads inside the three dimensional cavity of cryptand 1. The NOESY spectrum of the pseudorotaxane  $1 \supset 2$  in acetone- $d_6$  is presented in Fig. 5, wherein clear correlations may be seen between phenylene protons d and e of cryptand 1 and protons A and B of bipyridinium salt 2, confirming that bipyridinium salt 2 was incorporated within cryptand 1.

#### Cation induced switching studies

Subsequent to synthesis of the pseudorotaxane, we undertook investigations into the use of alkali metal cations to induce dissociation and subsequent displacement of the threaded component from the cryptand cavity. We anticipated that, upon addition of an alkali metal cation, the cryptand would preferentially coordinate to the cation, leading to displacement of the bipyridinium salt and a consequent change in the absorption spectrum of the complex.

When  $NaPF_6$  was added to an equimolar mixture (2 mM) of cryptand 1 and bipyridinium salt 2 in acetone, a



Fig. 5 Partial NOESY spectrum (300 MHz, acetone- $d_6$ , 293 K) of an equimolar mixture (50 mM) of 1 and 2

color change was observed from pale vellow to colorless. As shown in Fig. 6, the absorbance associated with the charge transfer band at about 380 nm in the UV-Vis spectrum decreases as the level of NaPF<sub>6</sub> increases, indicating that the addition of the cation results in the bipyridinium salt dethreading from the cryptand. Interestingly, adding one equivalent of Na<sup>+</sup> to the pseudorotaxane appears to have induced complete displacement, due to strong complexation of the Na<sup>+</sup> by the cryptand via the three dimensional electron-donating sidearms of the 15-crown-5 ring. Electrostatic repulsion between the bound Na<sup>+</sup> and the bipyridinium salt within the cavity of the cryptand evidently bring about the disassembly of the cryptand-based pseudorotaxane. It has therefore been demonstrated that this cryptand-based pseudorotaxane may act as a sensitive sensor for alkali metal cations via a color change.

This cation-induced dethreading behavior was also monitored by <sup>1</sup>H NMR. Figure 7 presents the <sup>1</sup>H NMR spectra of cryptand **1** (Fig. 7a), the pseudorotaxane formed from **1** with bipyridinium salt **2** (Fig. 7b), an equimolar mixture of NaPF<sub>6</sub> and the pseudorotaxane (Fig. 7c) as well as an equimolar mixture of NaPF<sub>6</sub> and **1** (Fig. 7d), all in acetone- $d_6$ . Upon addition of one equivalent (14 mM) of NaPF<sub>6</sub> to the pseudorotaxane, the chemical shifts corresponding to



**Fig. 6** *Top*: Photographs depicting the color of 10 mM solutions in acetone of **a 1**, **b** an equimolar mixture of **1** and **2** and **c** solution (**b**) upon addition of 1 equiv. of NaPF<sub>6</sub>; *bottom*: partial UV–Vis spectra of the titration of NaPF<sub>6</sub> into an equimolar solution of **1** and **2** (acetone, 2 mM)



**Fig. 7** Partial <sup>1</sup>H NMR spectra (300 MHz, acetone- $d_6$ , 293 K) of **a 1**, **b** an equimolar mixture (14 mM) of **1** and **2**, **c** solution (**b**) after addition of 1 equiv. of NaPF<sub>6</sub>, and **d** an equimolar mixture (14 mM) of **1** and NaPF<sub>6</sub>

phenylene protons d and e of cryptand 1 return to essentially the same values as their pre-complexed chemical shifts, as can be seen by comparing Fig. 7a-c, indicating that bipyridinium salt 2 was completely dethreaded from cryptand 1. The addition of NaPF<sub>6</sub> to the pseudorotaxane also results in chemical shifts corresponding to the oxyethylene protons of the crown ring and the benzylic methylene protons (f) which are practically identical to those obtained for the complex of cryptand 1 with Na<sup>+</sup> but without 2 in acetone- $d_6$ , as shown in Fig. 7c, d. This indicates that the Na<sup>+</sup> was indeed captured inside the cavity of cryptand 1 when added to the pseudorotaxane. These signal changes imply that the sodium cation becomes associated with the ether oxygen atoms in the 15-crown-5 ether moiety and consequently the bipyridinium salt 2 is dethreaded due to electrostatic repulsion forces, resulting in displacement-type molecular motion.

NMR titration experiments with the pseudorotaxane were conducted to determine if the particular alkali metal cation added had an effect on the extent to which the  $\pi$ electron interactions between the cryptand and the bipyridinium salt were disrupted. Solutions of KPF<sub>6</sub>, NaPF<sub>6</sub>, or LiPF<sub>6</sub> were titrated into a solution of the pseudorotaxane in acetone- $d_6$  with results as shown in Fig. 8. Interestingly, when either KPF<sub>6</sub> or NaPF<sub>6</sub> was titrated into the pseudorotaxane solution, signal changes for proton d reached saturation upon addition of equimolar amounts of either guest species. On the other hand, larger quantities of  $LiPF_6$ were required to achieve comparable degrees of replacement of the bipyridinium salt by the alkali metal cation. The dethreading process is therefore more effective when either K<sup>+</sup> or Na<sup>+</sup> is used, as compared to Li<sup>+</sup>, probably due to selectivity toward  $K^+$  and  $Na^+$  by the crown ether portion. Nevertheless, it is apparent that a variety of alkali



Fig. 8 <sup>1</sup>H NMR titration curves for KPF<sub>6</sub>, NaPF<sub>6</sub>, and LiPF<sub>6</sub> with an equimolar mixture (5 mM) of 1 and 2, monitoring proton d in acetone- $d_6$  at 293 K

metal cations are capable of dethreading bipyridinium salt **2** in this displacement system.

#### Conclusions

This work accomplished both the design and synthesis of a cryptand containing two electron-rich aromatic rings and able to bind bipyridinium derivatives. This cryptand structure has been shown to exhibit complexation behavior towards various bipyridinium salts by  $\pi$ -electron interactions and the resulting pseudorotaxane is capable of sensing alkali metal cations via a displacement mechanism. As a result, we have developed a simple synthetic strategy for a pseudorotaxane employing bipyridinium salts and have demonstrated the functioning of this pseudorotaxane as a chemosensor for alkali metal cations through the use of displacement assays.

We are currently extending this principle to other interlocked structures such as rotaxanes and catenanes which may be capable of providing shuttling [15-18] and rotating [59, 60] movements for molecular sensing applications, utilizing oxyethylene moieties as a binding site for cationic as well as neutral sensing targets.

#### Experimental

All chemicals were commercially available reagent grade and were used without further purification. The synthesis of *cis*-2,9-bis(bromomethyl)-2,9-dimethyl-15-crown-5 has been described previously [54]. The preparation of 1,8-bis[4-(hydroxymethyl)phenoxy]-3,6-dioxaoctane was carried out according to a previously reported procedure [55]. Bipyridinium salt derivatives **2**, **3**, and **4** were prepared according to published procedures [61–63]. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using a Varian Mercury 300 spectrometer with SiMe<sub>4</sub> as an internal standard. Mass spectra were obtained using a JEOL JMS-DX-303 mass spectrometer. Elemental analyses were performed using a Yanaco CHN-Corder MT-5 analyzer.

1,26-Dimethyl-3,9,12,15,18,24,27,30,33,35,38undecaoxa-5,8,19,22-dibenzobicyclo[24.7.6]nonatriacontane (1) [13, 16]

To a stirred suspension of 60 % NaH in oil (0.20 g, 5.0 mmol) in di(ethylene glycol) dimethyl ether (diglyme) (20 mL) under Ar, a solution of cis-2,9-bis(bromomethyl)-2,9-dimethyl-15-crown-5 [54] (0.52 g, 1.2 mmol) and 1,8-bis[4-(hydroxymethyl)phenoxy]-3,6-dioxaoctane [55] (0.51 g, 1.4 mmol) in diglyme (15 mL) was added dropwise over a period of 4 h at 120 °C. The resulting mixture was stirred for 79 h at 120 °C. After the mixture was cooled to room temperature, insoluble matter was removed by filtration through a Celite pad and the filtrate was subsequently evaporated under reduced pressure. The residue was purified by silica gel chromatography (eluent: hexane/ethyl acetate = 75/25) to afford cryptand 1 as a yellow oil (0.25 g, 33 %). <sup>1</sup>H NMR  $(300 \text{ MHz}, \text{CDCl}_3)$ :  $\delta$  (ppm) 1.18 (s, 6H), 3.28–3.67 (m, 20H), 3.74 (s, 4H), 3.85 (t, 4H, J = 4.8 Hz), 4.09 (t, 4H, J =4.8 Hz), 4.43 (d, 2H, J = 12 Hz), 4.48 (d, 2H, J = 12 Hz), 6.86 (d, 4H, J = 8.7 Hz), 7.19 (d, 4H, J = 8.7 Hz);<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 19.1, 62.4, 67.5, 69.8, 70.7, 70.8, 71.0, 72.8, 72.9, 73.2, 76.5, 114.5, 129.2, 130.6, 158.3; HRMS(FAB): m/z for M+H<sup>+</sup>: calculated: 635.3431; observed: 635.3428; elemental analysis calcd (%) for C<sub>34</sub>H<sub>50</sub>O<sub>11</sub>: C 64.33; H 7.94; found: C 64.09; H 8.01.

Determination of the association constants  $(K_a)$ 

All titration results were acquired using a Varian 300 MHz NMR spectrometer with the initial concentration of host 1 at 2.0 mM. Appropriate aliquots of guests 2, 3 and 4 as 54 mM solutions were added to the host solution with a microsyringe. Host protons (d) were monitored during the course of the titration. The complexation equilibrium was fast on the NMR time scale and signals were obtained as weight averaged chemical shifts of both the free and complexed host. The association constants  $(K_a)$  for the complexation processes were obtained by subjecting observed chemical shift changes from the titration experiments to non-linear least-squares data analysis using a 95 % confidence interval based on Student's t distribution, as reported by Hirose [58]. The volume change which occurs over the course of the titrations is accounted for in Hirose's method. The limiting chemical shifts,  $\Delta_0$ , meaning the difference in  $\delta$  values for the protons of the host **1** in the uncomplexed and fully complexed species, as well as the standard deviation and the curve fitting errors for the association constants, were determined by SOLVSTAT [64].

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