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Synthesis and complexing property of four-bridged crownopaddlanes

Seiichi Inokuma, Tomohiro Sakaizawa, Takashi Funaki, Tomomi Yonekura, Hiroko Satoh, Shin-ichi Kondo, Yosuke Nakamura and Jun Nishimura*

Department of Nano-material Systems, Graduate School of Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu 376-8515, Japan

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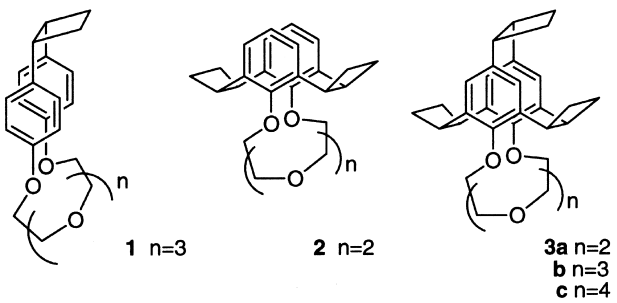
Abstract—A new series of crown compounds crownopaddlanes **3a**–**c** bearing three cyclobutane rings were prepared by means of intramolecular [2+2] photocycloaddition of styrene derivatives. The yield of crownopaddlane **3b** possessing five ethereal oxygen atoms was remarkably high 52% with the addition of sodium borofluoride in the photoreaction system. As this template effect suggests, **3b** showed extraordinarily high Na^+-selectivity with high efficiency on the liquid–liquid extraction of alkali metal picrates, though **3a** having four ethereal oxygen atoms did not extracted any cations in this system. The high Na^+-selectivity of **3b** was further clarified by the equilibrium stability constants (log K_a) for Na^+ (5.85) and K^+ (2.91) in acetonitrile solution. The complexation of **3b** to Na^+ cation was also examined by X-ray crystallography. Crownopaddlane **3c** bearing six ethereal oxygen atoms also efficiently and selectively extracted alkali metal cations, compared with conventional 18-crown-6 derivatives.

1. Introduction

Designing a host molecule preorganized for a certain guest is one of the most important strategies for increasing the complexing ability. The appropriate preorganization including rigdification results in a high substrate-selectivity with a large stability constant due to small entropy change before and after the complexation.[1,2] In regard to this, increasing attention has been focused on calixarene derivatives having rigid framework. In particular, calixcrown ethers have attracted intense interest as specific alkali metal cation reseptors.[3]

Making a sophisticated preorganized host, however, often results in a low overall yield because of the required multistep preparation. Recently, we have successfully synthesized crownophanes **1** by our efficient and versatile [2+2] photocycloaddition (yields were generally up to 95%).[4] In this case, template effect[5,6] and high dilution technique[7,8] are not indispensable. It has been also clarified that crownophanes **1** possessing five ethereal oxygen atoms exhibited higher complexing ability toward Li^+ ion on a solid–liquid extraction[9] and liquid membrane transport than conventional lithiophilic dibenzo-14-crown-4 due to the unique structure.[10] Furthermore, three-bridged crownopaddlane **2** possessing more rigid framework and efficiently prepared by the photoreaction, quantitatively and exclusively extracted Li^+ ion, preventing itself from making a 2:1 (host/guest) complex with large cations by its two cyclobutane blades,[11] though it did not work as an extractant in a liquid–liquid system.

In this paper, we report the photosynthesis of more rigid crownopaddlanes **3a**–**c** than **2** and their complexation properties. These crownopaddlanes are correspondent to homocalix[2]crown derivatives and are expected to show a specific affinity toward alkali metal cations due to their rigid structure possessing three cyclobutane ring as linkages.



2. Results and discussion

2.1. Synthesis of the crownopaddlanes

α,ω-Bis(2,4,6-tribromophenyl)oligo(oxyethylene)s were easily prepared by the conventional method and converted

Keywords: crown compounds; extraction experiment; photosynthesis; cyclophanes.
* Corresponding author. Tel.: +81-277-30-1310; fax: +81-277-30-1314; e-mail: nisimura@chem.gunma-u.ac.jp

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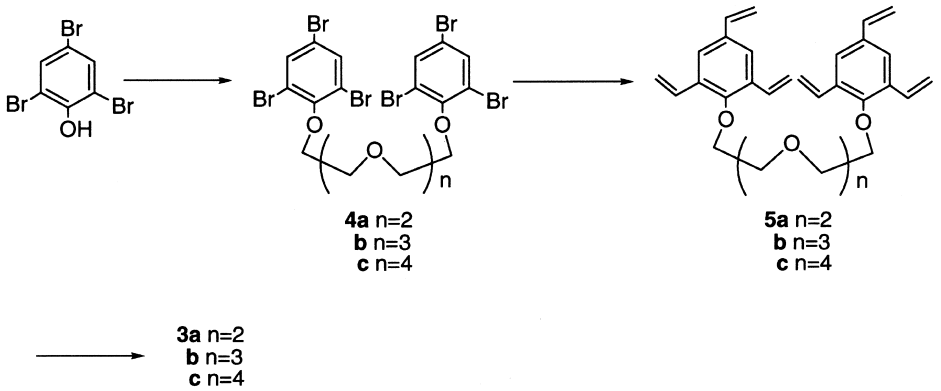


Scheme 1. Synthesis of the crownopaddlanes. *Reagents and conditions*: (a) $TsO(CH_2CH_2O)_{n+1}Ts$, CsF/MeCN, (b) $CH_2{=}CHSn(n\text{-}Bu)_3$, $Pd(PPh_3)_4$, 2,6-di-*tert*-butyl-4-methylphenol/toluene, (c) $h\nu$ (>280 nm)/solv. (MBF_4).

to the corresponding bis(trivinylphenyl) derivatives by Stille reaction.[12] In comparison with intermolecular triple [2+2] photoreaction of 1,3,5-trivinylbenzene (yields, 1%),[13] high yields (up to 18% even in the absence of a template salt) were recorded on the photocycloaddition of olefin **5**, indicating the favorable effect of the oligo (oxyethylene) linkage on the intramolecular reaction (Scheme 1).[14]

Two isomers from 1,3,5-trivinylbenzene were formed in the 1:3 ratio raised from the direction of cyclobutane blades,[13] while only one product was formed in this reaction from **5** to **3** due to the rigid viny group conformation caused by the steric hindrance of crown ether moiety. The structure of **3** was determined by ^{1}H NMR spectroscopic analysis (Fig. 1) where only two singlet peaks were observed in the aromatic region. The fact is consisted with the structure of three-bridged crownopaddlane **2** determined by X-ray crystallography.[11]

2.2. Solvent and template effects

To obtain target compounds in good yields, the reaction was carried out with or without a template in various solvents. Precursor **5b** was chosen as the representative olefin and the time-course of the reaction was followed by ^{1}H NMR spectra and HPLC analyses.

The yields of crownopaddlanes increased with the conversions of olefins and then reached plateau at around 1 h. In contrast to the photosynthesis of **2**,[11] it was not apparent whether the reaction yields clearly depended on the solvent polarity or not (Fig. 2). The yield in MeCN (Fig. 2(c)) was the lowest among all systems, though it was remarkably increased (up to 52%) by the addition of $NaBF_4$ (Fig. 2(f)), indicating that sodium cation efficiently acted as a template. On the contrary, the template effect was not ascertained in

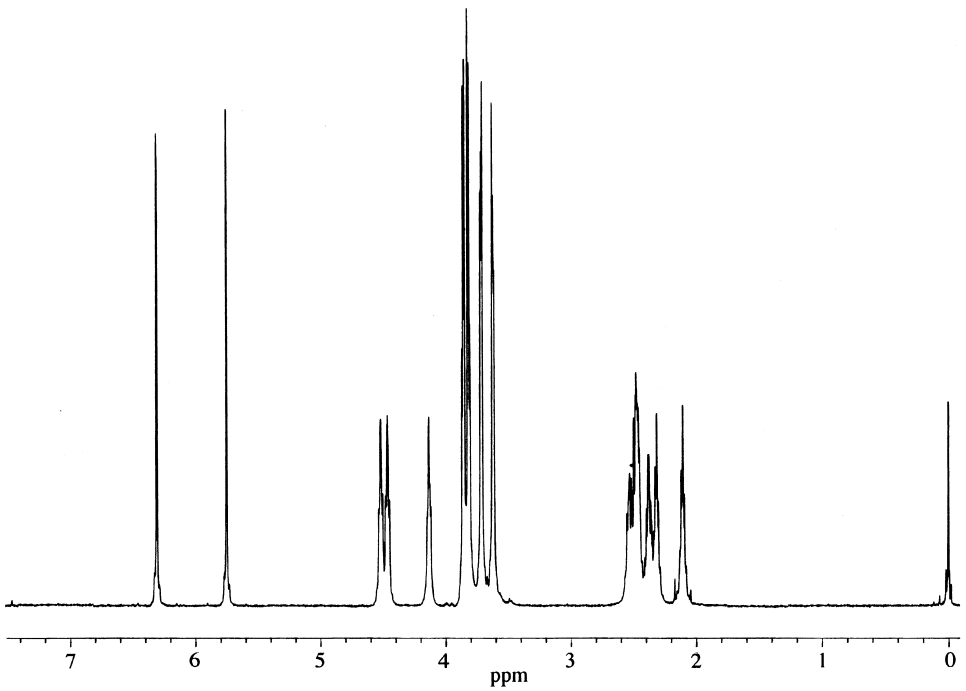


Figure 1. ^{1}H NMR spectrum of three bridged crownopaddlane **3b**.

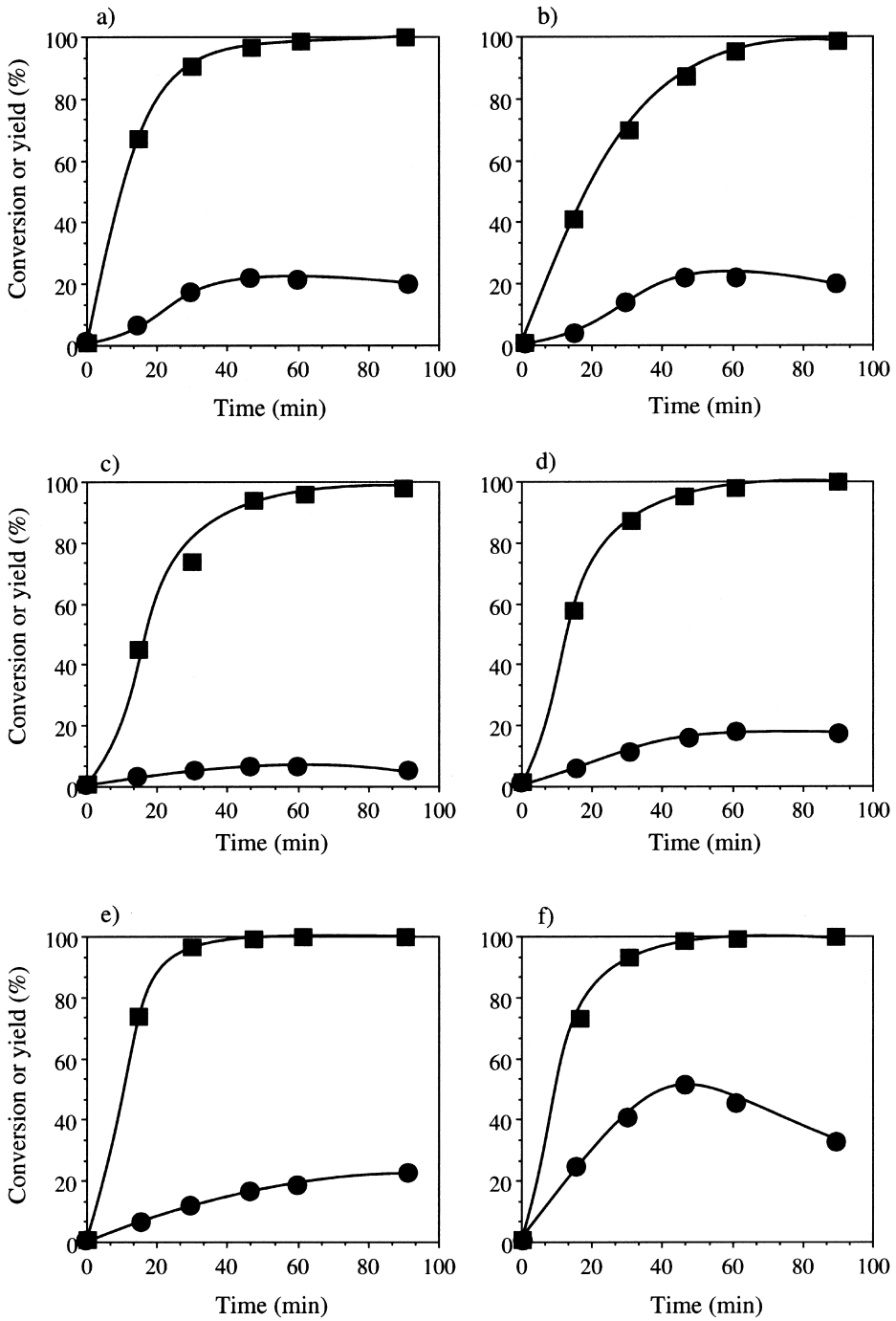


Figure 2. Solvent and template effect on the photocycloaddition of **5b**: (a) in cyclohexane, (b) in benzene, (c) in MeCN, (d) in MeOH, (e) in cyclohexane in the presence of $NaBF_4$, (f) in MeCN in the presence of $NaBF_4$. —■—, conversion; —●—, yield of **3b**.

cyclohexane because the solubility of the salt is extremely low in the solvent. Generally speaking, however, the oligo(oxyethylene) linkage of the olefin showed an extraordinarily large template effect on the intermolecular cyclization of the trivinylbenzene moieties.

2.3. Solvent extraction of alkali metal picrates by crown compounds

Extraction experiments were carried out in $H_2O-CH_2Cl_2$ and $H_2O-CHCl_3$ systems. As reported previously, three-bridged crownopaddlanes **2a–c** had showed high extractability in a solid–liquid extraction system, especially **2a** possessing four ethereal oxygen atoms had quantitatively and exclusively extracted Li^+ ion,[11] though crownopaddlane **2a** hardly extracted any alkali metal cations in the liquid–liquid extraction system.

Although four-bridged crownopaddlane **3a** having four ethereal oxygen atoms did not extract any cations, crownopaddlane **3b** possessing five ethereal oxygen atoms showed higher efficiency and selectivity toward Na^+ ion than conventional benzo-15-crown-5 **7**, which is known as Na^+-selective carrier. According to a space-filling model

examination, the rigid cavity size of **3b** (ca. 2.0 Å) kept by three cyclobutane bridges is quite suitable for Na^+ ion. Furthermore, its two cyclobutane blades located in the vicinity of phenolic oxygen atoms can effectively prevent it from forming a 2:1 (host/guest) sandwich complex with large cations, such as K^+, Rb^+ and Cs^+ ions.

The effective preorganization for **3b** to the cation was again emphasized, because the corresponding crownophane **6a** with relatively flexible three tetramethylene bridges showed no extractability at all. In general, crownopaddlane **3c** showed higher extractability, especially toward large cations, than benzo-18-crown-6 **8** and dibenzo-18-crown-6 **9**. In contrast with three tetramethylene-bridged crownophane **6b**[15] showing higher affinity toward the largest Cs^+ ion, the trend of extractability of crownopaddlane **3c** was similar to **8** and **9**.

2.4. Complexation of crownopaddlane 3b with alkali metal cations in homogeneous solution

Electrospray ionization mass spectroscopy (ESI-MS) is one of the most simple and useful method to disclose the complexing behavior of host compounds with cations in a polar homogeneous system.[16] The interaction between the paddlane and alkali metal perchlorates were investigated in competitive system in CH_3CN-H_2O (4:1, v/v) solution.

As shown in Figure 3, **3b** was almost completely consumed by complexation since the $[M]^+$ was hardly detected and the paddlane formed only the 1:1 complex with each cation with Na^+-selectivity. In contrast with **3b**, conventional benzo-15-crown-5 **7** formed the 1:1 and 2:1 (host/guest) complexes with all alkali metal cations as shown in Figure 4. Thus, it was found that paddlane **3b** showed unique complexing behavior.

2.5. Determination of association constants (K_a)

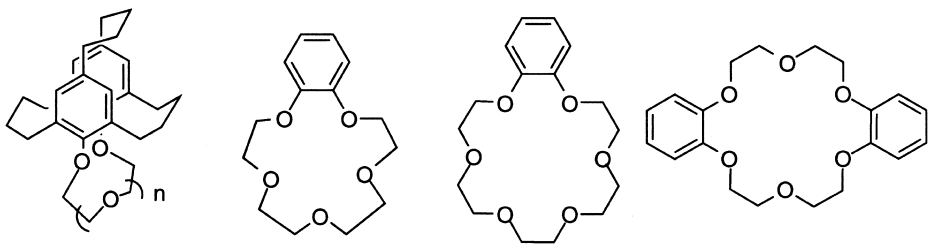
Information regarding Na^+/K^+ discrimination ability is very valuable in applications for biological field. Thus, ^1H NMR titration with sodium and potassium perchlorate was carried out in acetonitrile-d_3 at 25°C to assess in detail the binding ability of **3b** since, it showed high Na^+ ion-selectivity on the liquid–liquid extraction (Table 1) and ESI-MS analysis (Fig. 3). Although 15-crown-5 is considered to be favorable for incorporating Na^+ ion from the size-fitting concept, it shows not only poor selectivity Na^+ over K^+ ion but rather K^+ ion-selectivity against Na^+ ion as shown in Table 2. In contrast to the selectivity of the conventional 15-crown-5 ether, crownopaddlane **3b** showed extraordinarily high Na^+ ion-selectivity against K^+ ion, which is comparable to those of calix[4]crown compounds[17] and calix[4]arene derivatives.[18] This is again caused by the rigid structure due to multi-bridging cyclobutane rings with steric hindrance to form only 1:1 complexation.

2.6. Crystal structure of crownopaddlane 3b

The specific complexation feature mentioned above was examined by X-ray crystallographic analysis. Single crystals of the complex between **3b** and sodium picrate were obtained from methanol solution.

As illustrated in Figure 5, the solid state structure of Na^+-**3b** complex is actually assessed to have the structural rigidity and the two bulky cyclobutane blades attached to 2- and 6-posision of the each aromatic nuclei clearly show to be able effectively prevent itself from forming a 2:1 (host/guest) sandwich complex as examined by space-filling model. The sodium cation is surrounded by the five ethereal oxygens and one methanol molecule with Na–O(1) 2.45, Na–O(2) 2.37, Na–O(3) 2.49, Na–O(4) 2.38, and Na–O(5)

Table 1. Liquid–liquid extraction of metal picrate with crownopaddlanes



Ligand	Percent extraction				
	Li^+	Na^+	K^+	Rb^+	Cs^+
3a[a]	0	0	0	0	0
3b[a]	1	10	2	1	1
3b[b]	0	24	3	0	0
3c[a]	0	4	47	42	31
6a[a]	1	2	20	39	47
7[a]	2	4	6	5	3
7[b]	1	12	6	5	1
8[a]	1	5	56	38	21
9[a]	1	2	34	20	10

Extraction conditions: aqueous phase, [MOH]=0.1 M, [picric acid]=5.0×10^{-5} M, 5 mL. Organic phase, 5 mL.
[a] [ligand]=5.0×10^{-5} M, CH_2Cl_2.
[b] [ligand]=5.0×10^{-4} M, $CHCl_3$. Determined by UV–vis specroscopy.

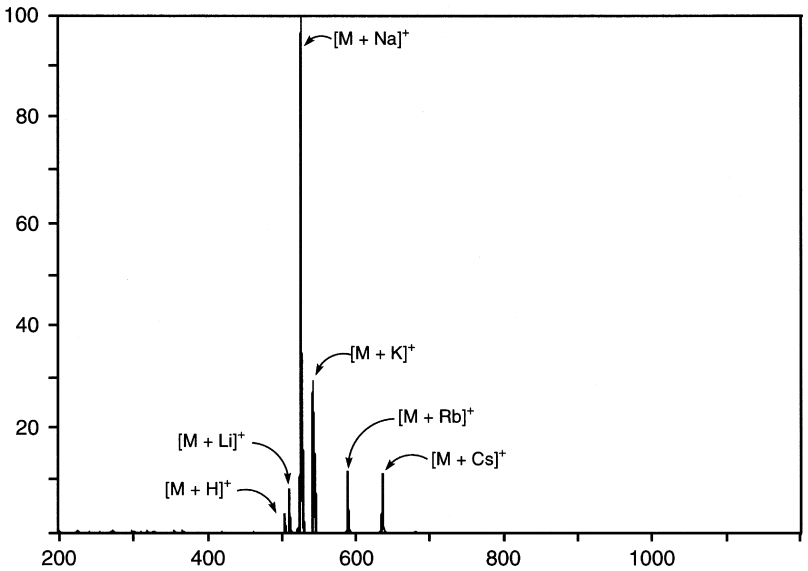


Figure 3. ESI-MS spectrum of **3b** in 4:1 (v/v) $CH_3CN–H_2O$ containing equimolar mixture of $LiClO_4$, $NaClO_4$, $KClO_4$, $RbClO_4$, and $CsClO_4$.

2.39 Å, and the angle O(1)–Na-(2), O(2)–Na-(3), O(3)–Na-(4), O(4)–Na-(5), and O(5)–Na-(1) are 70.4, 68.3, 69.1, 71.7, 80.1°, respectively. The five oxygen atoms are nearly coplanar and the sodium cation is 0.27 Å from this plane toward the methanol molecule with Na–O(13) 2.43 Å. Thus, the arrangement of oxygens around the sodium cation is a distorted pentagonal pyramidal configuration. This complexation feature is quite similar to that of sodium iodide-benzo-15-crown-5 complex formed in methanol system, in which sodium cation is coordinated to one oxygen atom of water as well as the five ethereal oxygen atoms, and the cation does not interact with the anion.[20]

Although Na^+-**3b** complex possess a picrate anion, the complexation manner differs from that of sodium picrate-benzo-15-crown-5 complex,[21] in which sodium cation is coordinated to the five ethereal oxygen and the phenoxide anion. In the latter case, the picrate anion prevents the cation from the coordination of not only one ethanol molecule but also one water molecule due to its sufficiently high nucleophilicity even when the crystallization has been carried out in ethanol containing up to 20 vol.% of water. In spite of this high nucleophilicity of a picrate anion, the sodium cation does not react with the picrate anion, but reacts with one methanol molecule in the present case,

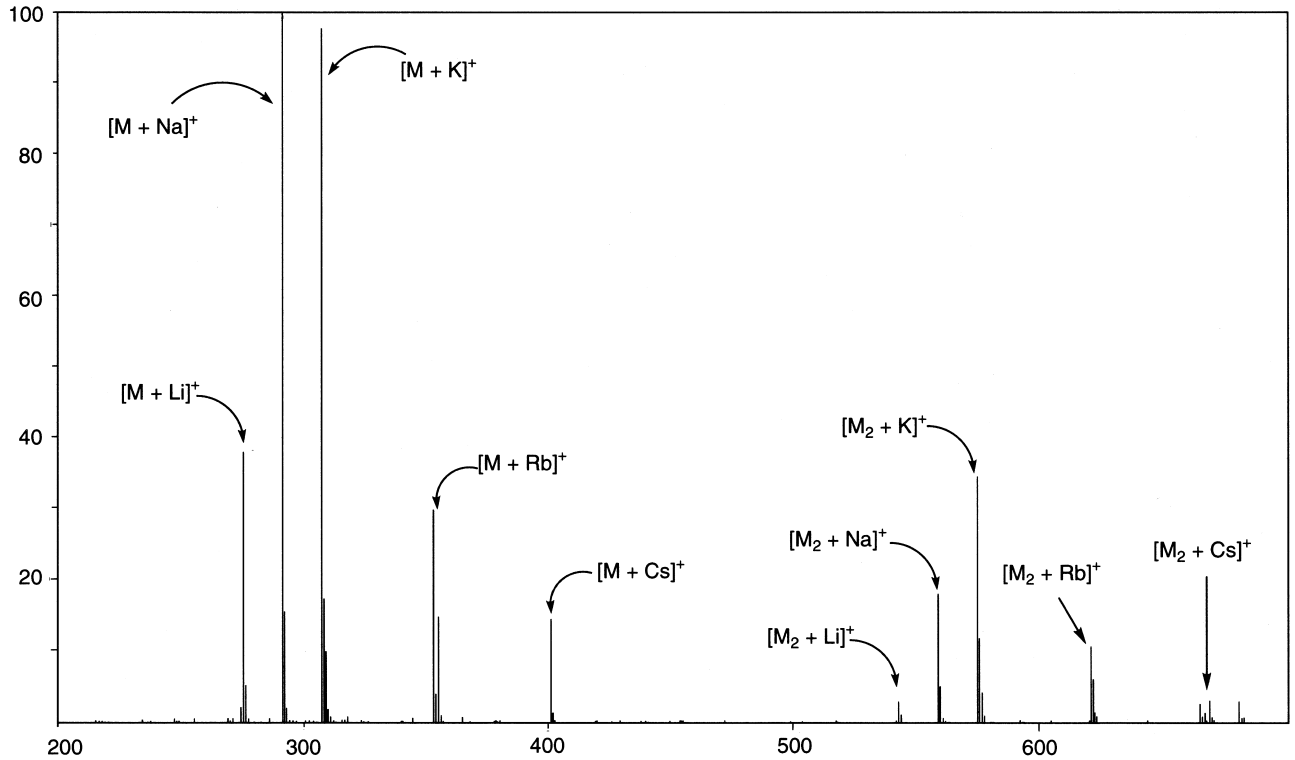
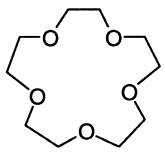


Figure 4. ESI-MS spectrum of **7** in 4:1 (v/v) $CH_3CN–H_2O$ containing equimolar mixture of $LiClO_4$, $NaClO_4$, $KClO_4$, $RbClO_4$, and $CsClO_4$.

Table 2. Complexing stability constants of crown compounds with Na^+ or K^+



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Crown compounds	log K_a		Selectivity
	Na^+	K^+	Na^+/K^+
3b[a]	5.85	2.91	871
10[b,c]	3.48	3.77	0.51

[a] In MeCN-d_3.
[b] In MeOH.
[c] Ref. 19.

suggesting that the two bulky cyclobutane blades attached to 2- and 6-position of the each aromatic nuclei effectively prevent the cation from the coordination of the bulky picrate anion. Consequently, the picrate anion lies close to 3- and 3′-protons of aromatic nuclei of **3b** most likely due to an edge-to-face interaction with aromatic nuclei of **3b**.

3. Conclusion

The crownopaddlanes were conveniently synthesized by means of intramolecular [2+2] photocycloaddition of trivinylbenzene derivatives. These crown compounds are correspondent to rigid calix[2]crown derivatives due to possessing three cyclobutane ring as linkages. In regard with the binding properties, it is noteworthy that paddlane **3b** shows remarkably high Na^+-selectivity in the extraction experiment and homogeneous systems.

4. Experimental

4.1. General remarks

Elemental analysis was carried out in Technical Research Center for Instrumental Analysis, Gunma University. ^1H NMR spectra were recorded on a JEOL α-500 FT NMR spectrometer. HPLC analysis was performed with a Shimadzu LC-6A pump, an LC-6A UV detector, and an RC-4A data processor. UV–vis spectra were recorded by a Hitachi U-3210 spectrophotometer. Electrospray ionization mass spectra (ESI-MS) were obtained on a Perkin–Elmer Sciex API-100 electrospray ionization mass spectrometer under the following conditions: a sample solution was sprayed at a flow rate of 2 μL min^{-1} at the tip of a needle biased by a voltage of 4.5 kV higher than that of a counter electrode.

Cyclohexane, benzene, and toluene were distilled over Na after a prolonged reflux under a nitrogen atmosphere. Guaranteed reagent grade acetonitrile, methanol, CH_2Cl_2, and $CHCl_3$ were, distilled before use.

Four-bridged crownophane **6a**,**b**[15] were prepared by our method reported previously. Reagent grade benzo-15-crown-5, benzo-18-crown-6, and dibenzo-18-crown-6 were used without further purification. Commercially available highest grade alkali metal hydroxides were used. Picric acid was purified by recrystallization from acetone. All aqueous solutions were prepared with distilled, deionized water.

4.2. Synthesis of four-bridged crownopaddlanes

4.2.1. Preparation of α,ω-bis(2,4,6-tribromophenyl)oligo(oxyethylene)s 4a–c. To a suspension of CsF (0.379 mol) in 500 mL acetonitrile a mixture of 2,4,6-tribromophenol

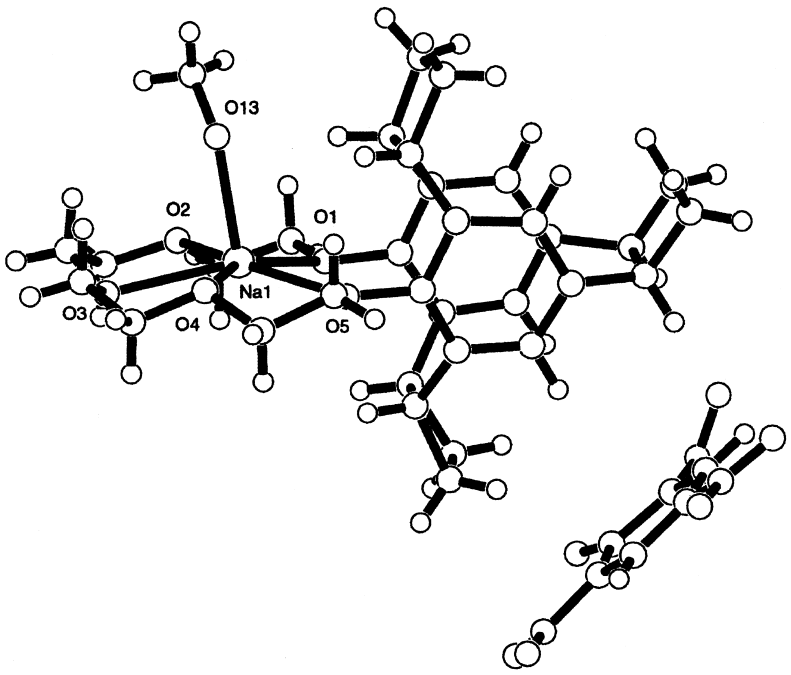

Figure 5. Crystal structure of sodium picrate-**3b** complex. Selected bond distances (Å) and angles (deg): Na–O(1) 2.45; Na–O(2) 2.37; Na–O(3) 2.49; Na–O(4) 2.38; Na–O(5) 2.39; O(1)–Na–O(2) 70.4; O(2)–Na–O(3) 68.3, O(3)–Na-(4) 69.1; O(4)–Na–O(5) 71.7; O(5)–Na–O(1) 80.1.

(0.126 mol) and corresponding oligoethyleneglycol ditosylate (0.06 mol) in acetonitrile (100 mL) was added at room temperature for 1 h under a nitrogen atmosphere. The mixture was stirred for 5 h under refluxing. The suspension was filtered and the filtrate was concentrated in vacuo. The residue was dissolved in CH_2Cl_2 and then successively washed with 10% aqueous sodium hydroxide and water, dried over magnesium sulfate. The organic layer was evaporated under reduced pressure to obtain the desired compounds.

Compound **4a**: yield, 89%; mp 76.0–77.0°C (acetone–hexane). ^{1}H NMR ($CDCl_3$); 7.65 (4H, s), 4.12–4.07 (4H, m), 3.99–3.96 (4H, m), 3.91–3.88 (4H, m). Calcd for $C_{18}H_{16}O_4Br_6$: C, 27.87; H, 2.08. Found: C, 27.65; H, 2.26.

Compound **4b**: yield, 96%; mp 66–67°C (acetone–hexane). ^{1}H NMR ($CDCl_3$); 7.64 (4H, s), 4.23–4.14 (4H, m), 3.97–3.88 (4H, m), 3.81–3.67 (8H, m). Anal. calcd for $C_{20}H_{20}O_5Br_6$: C, 29.30; H, 2.46. Found: C, 29.15; H, 2.61.

Compound **4c**: yield, 90%; viscous liquid (purified by silica gel column chromatography using a gradient mixed solvent of benzene and acetone). ^{1}H NMR ($CDCl_3$); 7.64 (4H, s), 4.20–4.13 (4H, m), 3.95–3.87 (4H, m), 3.80–3.63 (12H, m). Anal. calcd for $C_{22}H_{24}O_6Br_6$: C, 30.59; H, 2.80. Found: C, 30.38; H, 2.91.

4.2.2. Preparation of α,ω-bis(2,4,6-trivinylphenyl)oligo(oxyethylene)s 5a–c. A solution of α,ω-bis(2,4,6-tribromophenyl)oligo(oxyethylene) (11.0 mmol), tributylvinylstanane (0.822 mol), $Pd(PPh_3)_4$ (1.50 g, 1.30 mmol), and 2,6-di-*tert*-butyl-4-methylphenol (15 mg) in toluene was heated to reflux for 20 h. After the mixture was cooled to ambient temperature, large excess of 1.2 M aqueous KF solution was added, and the resulting mixture was stirred overnight at the same temperature. The organic layer was separated from sludgy and aqueous layer and then dried on magnesium sulfate. The concentrated crude material was purified by silica gel column chromatography using a gradient mixed solvent of benzene and acetone to afford the hexavinyl derivatives.

Compound **5a**: yield, 20%; viscous liquid. ^{1}H NMR ($CDCl_3$); 7.51 (4H, s), 7.07 (4H, dd, J=12.5, 17.5 Hz), 6.69 (2H, dd, J=12.5, 17.5 Hz), 5.41–5.32 (6H, m), 5.18–5.09 (6H, m), 4.01–3.96 (4H, m), 3.93–3.85 (8H, m). Anal. calcd for $C_{30}H_{34}O_4$: C, 78.57; H, 7.47. Found: C, 78.41; H, 7.59.

Compound **5b**: yield, 26%; viscous liquid. ^{1}H NMR ($CDCl_3$); 7.47 (4H, s), 7.07 (4H, dd, J=11.0, 17.7 Hz), 6.69 (2H, dd, J=11.0, 17.7 Hz), 5.80–5.68 (6H, m), 5.34–5.22 (6H, m), 3.96–3.92 (4H, m), 3.81–3.72 (12H, m). Anal. calcd for $C_{32}H_{38}O_5$: C, 76.47; H, 7.62. Found: C, 76.35; H, 7.71.

Compound **5c**: yield, 40%; viscous liquid. ^{1}H NMR ($CDCl_3$); 7.47 (4H, s), 7.06 (4H, dd, J=10.9, 17.7 Hz), 6.69 (2H, dd, J=10.9, 17.7 Hz), 5.82–5.67 (6H, m), 5.36–5.19 (6H, m), 3.96–3.92 (4H, m), 3.80–3.76 (4H, m), 3.74–3.68 (12H, m). Anal. calcd for $C_{34}H_{42}O_6$: C, 74.70; H, 7.74. Found: C, 74.51; H, 7.83.

4.2.3. Preparation of crownopaddlanes 3a–c. Into a 500 mL Pyrex flask with a magnetic stirrer and N_2 inlet was placed 0.5 mmol of α,ω-bis(2,4,6-trivinylphenyl)oligooxyethylenes **5** dissolved in acetonitrile (500 mL) and then nitrogen was bubbled for 15 min. The solution was irradiated by a 400-W high-pressure mercury lamp. The progress of the reaction was followed by HPLC. After irradiation for 2 h, the reaction mixture was evaporated. The crude reaction product was purified by silica gel column chromatography with a gradient solution of benzene–acetone to afford the crownopaddlanes.

Compound **3a**: yield, 17%; mp 174–175°C (methanol). ^{1}H NMR ($CDCl_3$); 6.33 (2H, d, J=2.1 Hz), 5.77 (2H, d, J=2.1 Hz), 4.56–4.40 (4H, m), 4.16–4.09 (2H, m), 3.99–3.95 (4H, m), 3.78–3.57 (8H, m), 2.59–2.28 (10H, m), 2.16–2.09 (2H, m). Anal. calcd for $C_{30}H_{34}O_4$: C, 78.57; H, 7.47. Found: C, 78.39; H, 7.55.

Compound **3b**: yield, 10%; mp 150–151°C. (methanol). ^{1}H NMR ($CDCl_3$); 6.31 (2H, d, J=2.1 Hz), 5.75 (2H, d, J=2.1 Hz), 4.61–4.39 (4H, m), 4.18–4.06 (2H, m), 3.89–3.55 (16H, m), 2.64–2.06 (12H, m). Anal. calcd for $C_{32}H_{38}O_5$: C, 76.47; H, 7.62. Found: C, 76.22; H, 7.74.

Compound **3c**: yield, 18%; mp 105–106°C. (methanol). ^{1}H NMR ($CDCl_3$); 6.30 (2H, d, J=2.1 Hz), 5.74 (2H, d, J=2.1 Hz), 4.57–4.44 (4H, m), 4.12–4.10 (2H, m), 3.88–3.57 (20H, m), 2.58–2.27 (10H, m), 2.14–2.06 (2H, m). Anal. calcd for $C_{34}H_{42}O_6$: C, 74.70; H, 7.74. Found: C, 74.48; H, 7.81.

4.3. Crystallographic structural determination of Na^+-3b complex

A methanol solution of (0.50 mL) of sodium picrate monohydrate (2.14 mg, 0.008 mmol) was added to a methanol solution of (0.50 mL) of **3b** (2.01 mg, 0.004 mmol) under nitrogen. The reaction mixture was allowed to stand at ambient temperature for a day. By slow evaporation of the solvent under nitrogen, crystallization yielded yellow prismatic crystals of sodium picrate-**3b** complex with a methanol molecule as a ligand. Mp 157–158°C. X-Ray crystallographic data were obtained on a Rigaku AFC7S instrument. Structures were solved by direct method and expanded using fourier techniques (DIRDIF-94 program system). Crystal, data collection, and refinement parameters are given in Table 3.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 218106. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

4.4. Solvent and additive effects on the photocycloaddition

The yields for photocyclization were measured under a variety of conditions by using a merry-go-round apparatus. The 15 mL Pyrex test tubes containing a solution of the precursor olefin (2 mmol dm^{-3}) with or without $NaBF_4$ (30 equiv.) in a degassed solvent were set around a 400-W high-pressure mercury lamp at the distance of 5 cm. After the irradiation for prescribed time, the olefin conversion and

Table 3. Crystal data and summary of X-ray experimental conditions for compound **3b**

Formula	$C_{39}H_{44}N_3O_{13}Na$
Formula weight	785.77
Temperature (°C)	20.0
$F(000)$	1584
Crystal size (mm^3)	0.20×0.25×0.30
μ (mm^{-1})	0.112
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	14.560(3)
b (Å)	15.226(3)
c (Å)	16.846(3)
β (°)	100.14(2)
V (Å)	3676(1)
Z	4
D (calc, g/cm^3)	1.420
2θ max (°)	55.0
Reflections collected	7308
Independent data	6691 (R_{int}=0.089)
R_1 [$I>2\sigma(I)$]	0.091
wR_2 (all data)	0.224
Goodness of fit on F^2	1.10

product yields were determined by HPLC and ^{1}H NMR spectroscopy.

4.5. Liquid–liquid extraction of alkali metal picrates

Crownopaddlane was used as an extractant for alkali metal picrates in a liquid–liquid system together with reference compounds. A CH_2Cl_2 or $CHCl_3$ solution of the host compound (1×10^{-5} mol dm^{-3} or 1×10^{-4} mol dm^{-3}, 5 mL) and an aqueous metal picrate solution ([MOH]=0.1 mol dm^{-3}, [picric acid]=1×10^{-5} mol dm^{-3}, 5 mL) were shaken in a 20-mL test tube equipped with a ground glass stopper at room temperature (20–22°C) for 2 h. After two liquid phase were separated, percent extraction of metal picrates were measured by UV–vis spectroscopy.

4.6. ^{1}H NMR titration of crownopaddlane 3b with sodium perchlorate and potassium perchlorate

An acetonitrile-d_3 solution of **3b** (1 mmol dm^{-3}) was prepared, and its 500 μL portions was placed in an NMR tube, and the solvent level was marked. A second solution was made in acetonitrile-d_3 with the metal perchlorate. An initial spectrum was recorded, then an appropriate volume of the salt solution was added to the NMR tube and the solvent level was reduced by evaporation to the mark. The spectrum was then recorded again. This procedure was repeated until the salt concentration is reached ten equivalent of that of the crownophane. The chemical shifts of the aromatic proton of **3b** before and after each addition of the guest solution were used for calculation of the association constants (K_a). The constants were determined by non-linear least-squares fitting method of the titration curves for 1:1 complexation, which was monitored by the ESI-MS analysis (Fig. 4).

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