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Synthesis of crownophanes possessing three pyridine rings

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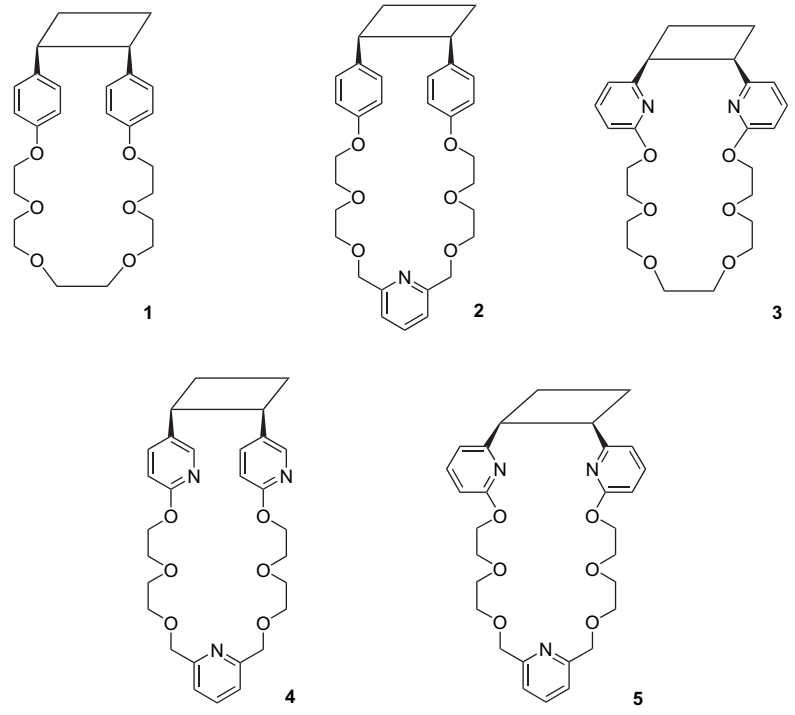
Abstract—Novel crownophanes with three pyridine moieties (pyridinocrownophanes **4** and **5**) were prepared by means of intramolecular [2+2] photocycloaddition of vinylpyridine derivatives. In the liquid–liquid extraction of heavy metal cations, **4** and **5** exhibited high efficiency toward Ag^+. Comparing the high extractability and complexing stability constant for Ag^+ to those of the corresponding pyridinocrownophanes **2** and **3** and observing the ^1H NMR spectra in the presence of Ag^+, the ethereal oxygen atoms and the three nitrogen atoms were found efficiently and cooperatively to act as ligating sites.

1. Introduction

Within the last three decades macrocycles containing pyridine moieties in the polyether ring, pyridinophanes, attracted much interest from the structural and functional points of view. These compounds were extensively investigated by Vögtle[1–4] and Newkome[5–9] as host molecules in earlier works.

In particular, the pyridinophanes has been reported to act as ligands for silver cation in many papers.[10–24] We have already prepared some crown compounds[25–27] possessing pyridine residues as ligating side arms on the hydroxycrownophanes, which were prepared by the intramolecular [2+2] photocycloaddition of styrene derivatives in a manner similar to typical crownophane (**1**).[28] We also prepared pyridinocrownophanes **2** and **3**, which have pyridine residues



Keywords: Crown compound; Cyclophane; Extraction; Ag^+-selective ionophore; [2+2] Photocycloaddition.
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located in the polyether linkage or on the cyclobutane ring.[29,30]

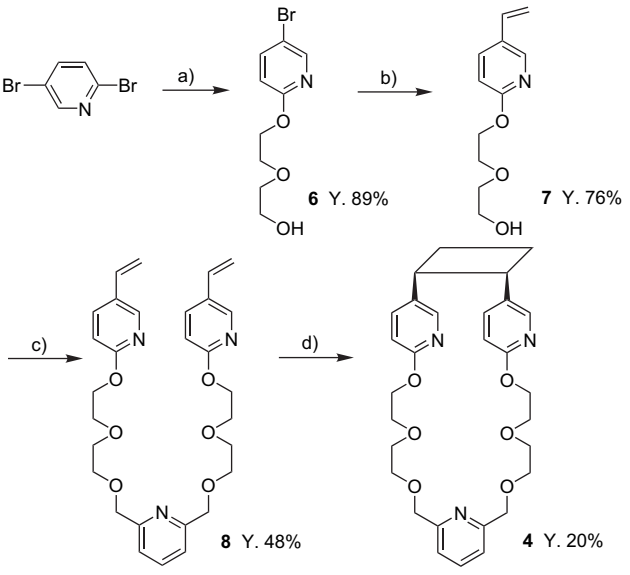
Comparing the complexing ability toward Ag^+ ion of these pyridinophanes, **2** was superior to **1**, which hardly extracted Ag^+ ion in a liquid–liquid system. Furthermore, pyridinocrownophane **3** was found to show moderate affinity toward Ag^+ ion in the liquid–liquid extraction. In order to achieve high Ag^+-affinity of pyridinocrownophanes, we designed pyridinocrownophanes **4** and **5** as hybrid type of pyridinophanes between **2** and **3**. Thus, in this paper we demonstrate the preparation and complexing behavior toward Ag^+ ion of pyridinocrownophanes **4** and **5** bearing three pyridine residues connected by the polyether linkage.

2. Results and discussion

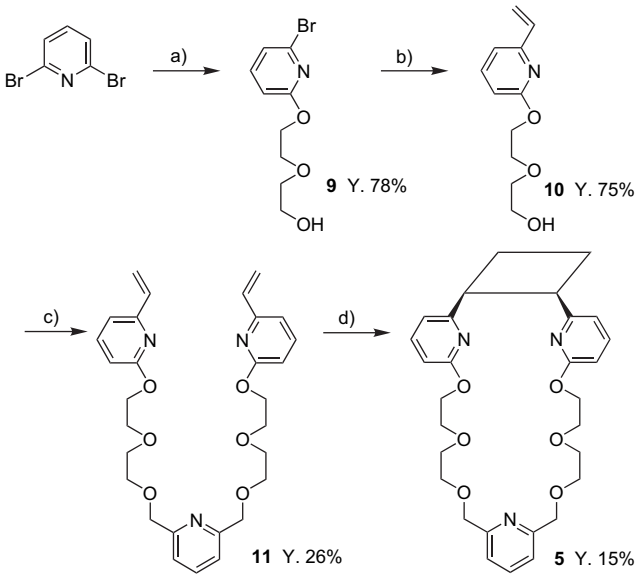
2.1. Synthesis of pyridinocrownophanes (4 and 5)

Synthetic routes of pyridinocrownophanes **4** and **5** were shown in Schemes 1 and 2. Precursor olefins **8** and **11** were prepared from the reaction between 2,6-bis(tosyloxymethyl)pyridine and diethylene glycol mono(vinylpyridyl) ethers **7** and **10**, which were obtained by Stille reaction[31] of the corresponding bromopyridine derivatives **6** and **9**, respectively. The photocycloaddition of **8** and **11** was carried out under the irradiation using a 400-W high-pressure mercury lamp through a Pyrex filter.

From ^{1}H NMR analysis pyridinocrownophanes **4** and **5** were found to have cis-cyclobutane ring, which was proved by the specific methine proton signals at δ 3.95–4.03 (in $CDCl_3$).[32] As shown in Figure 1 representative pyridinocrownophane **5** showed three sets of pyridine proton peaks (H_c, H_d, and H_e), which were assigned to those of pyridine rings on the cyclobutane ring on the basis of the spectral data of **3**.[30] The other pyridine proton peaks (H_a and H_b) were assigned to those of pyridine ring at the center of the polyether linkage based on



Scheme 1. Synthesis of pyridinocrownophanes. Reagents and conditions: (a) $HO(C_2H_4O)_2H$, NaH/THF. (b) CH_2=CHSn(*n*-Bu)$_3$, $Pd(PPh_3)_4$, 2,6-di-*tert*-butyl-4-methylphenol/toluene. (c) 2,6-Bis(tosyloxymethyl)pyridine, NaH/THF. (d) *hν* (>280 nm)/MeCN.



Scheme 2. Synthesis of pyridinocrownophanes. Reagents and conditions: (a) $HO(C_2H_4O)_2H$, NaH/THF. (b) CH_2=CHSn(*n*-Bu)$_3$, $Pd(PPh_3)_4$, 2,6-di-*tert*-butyl-4-methylphenol/toluene. (c) 2,6-Bis(tosyloxymethyl)pyridine, NaH/THF. (d) *hν* (>280 nm)/MeCN.

the integral ratio (1:2) and the coupling constants. These protons were also assigned in comparison with the spectrum of **3**, which does not have the corresponding pyridine nucleus. All pyridine protons were high-field shifted compared to those of the precursor olefins **8** and **11**, indicating the phane structure.

2.2. Complexing behavior of pyridinocrownophanes toward heavy metal cations

The liquid–liquid extraction of heavy metal cations by pyridinocrownophanes **4** and **5** was carried out together with crownophane **1**, pyridinocrownophanes **2** and **3**, and dibenzopyridino-18-crown-6 (**12**) as reference compounds. Crownophane **1** showed specific affinity toward alkali metal cations as reported previously,[28] but it exhibited very low extractability to heavy metal cations as shown in Table 1. The extractability of pyridinocrownophane **2** was significantly higher than that of **1**. This is considered to be due to chelate effect by the most stable double five-membered-chelate rings, which formed from the pyridine nitrogen and the two oxymethyl oxygen atoms attached at 2- and 6-position of the pyridine ring (Fig. 2). It has been previously reported that the ethereal oxygen atoms and the two nitrogen atoms in the pyridine ring of pyridinocrownophane **3**[26] acted as effective ligating sites cooperatively. Thus, we designed pyridinocrownophanes **4** and **5** having pyridine rings on the cyclobutane ring and the pyridine ring, which forms the five-membered-chelate rings, in the polyether linkage to obtain high complexing ability toward Ag^+ ion. In fact, pyridinophanes **4** and **5** showed extraordinarily high Ag^+-extractability. Their ability was higher than that of reference **12**. This indicates that the pyridine residue in the polyether linkage cooperatively acted with the two pyridine rings attached to the cyclobutane ring. The extractability of **3** without pyridine nucleus at the center of the polyether linkage was higher than that of the regioisomer having 2,5-pyridine moieties.[33] This agrees with the results of the space-filling model examination that **3** is more suitable to Ag^+ complexation than the

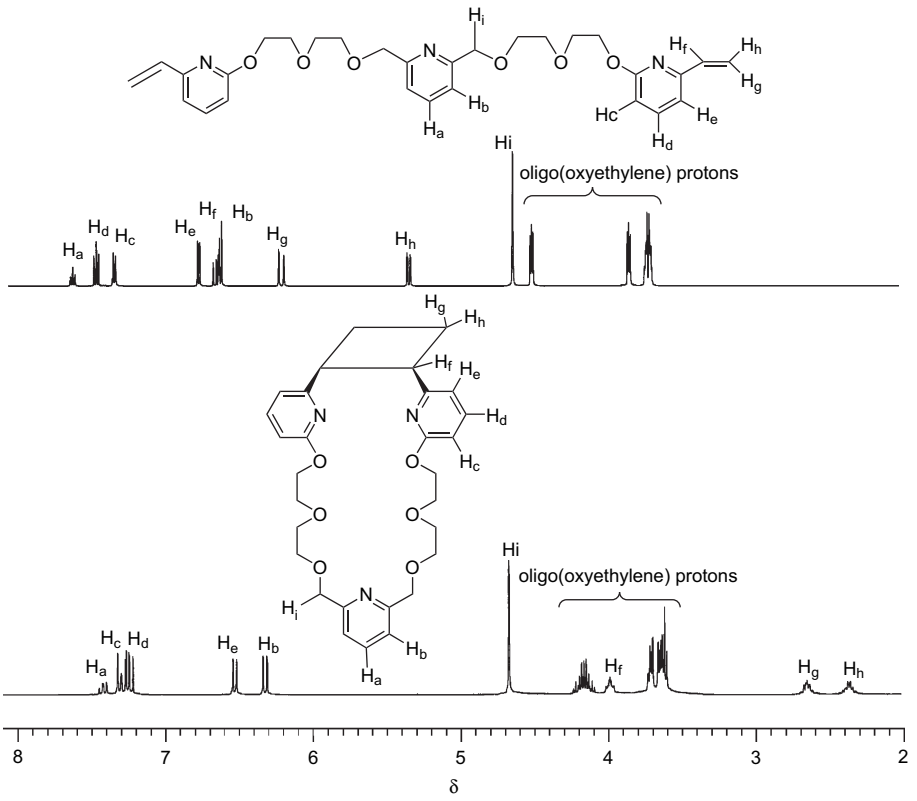
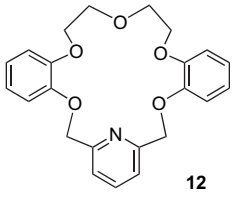


Figure 1. ^{1}H NMR spectra of pyridinocrownophane **5** and the precursor vinylpyridine derivative **11** in $CDCl_3$.

Table 1. Extraction of heavy metal cations by ligands[a]

Ligand	Extraction (%)							
	Ag^+	Pb^{2+}	Cu^{2+}	Mn^{2+}	Zn^{2+}	Ni^{2+}	Co^{2+}	Fe^{3+}
1	2 (4.1)	0 (5.0)	0 (4.5)	0 (6.8)	0 (6.2)	0 (6.4)	0 (6.5)	0 (1.5)
2	42 (5.4)	14 (5.4)	0 (5.0)	0 (6.3)	0 (6.4)	0 (6.6)	0 (7.3)	0 (2.0)
3	23 (5.6)	0 (4.7)	0 (4.4)	0 (6.6)	0 (6.1)	0 (6.0)	0 (6.6)	0 (1.6)
4	92 (5.2)	2 (4.9)	0 (4.5)	0 (6.8)	0 (6.4)	0 (6.5)	0 (6.6)	0 (1.6)
5	93 (4.9)	32 (4.8)	0 (4.5)	0 (6.8)	0 (6.3)	0 (6.6)	0 (67)	0 (1.7)
12	59 (5.5)	10 (5.6)	0 (4.1)	0 (6.3)	0 (6.2)	0 (6.7)	0 (6.9)	0 (1.6)

[a] Extraction conditions: aqueous phase (5 mL), [metal nitrate]=1.0×10^{-1} mol dm^{-3}; organic phase, CH_2Cl_2 (5 mL), [ligand]=1.0×10^{-4} mol dm^{-3}; ca. 20 °C, shaken for 1.5 h. The values were based on the concentration of the host compounds. Values in parentheses were equilibrium pH of aqueous phase.



12

isomer. On the other hand, both the extractability and the stability constant of pyridinophane **4** were almost the same as those of **5** listed in Tables 1 and 2 though different binding positions of cyclobutane ring on the pyridine rings. This suggests that the contribution of the pyridine ring at the center of the polyether linkage to Ag^+ complexation is larger than that of pyridine rings on the cyclobutane ring. This extraordinarily large contribution is again considered to be caused by the most stable five-membered chelation as shown in Figure 2.

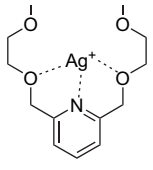


Figure 2. The most stable five-membered chelation to Ag^+ ion.

Table 2. Stability constant (K_a)[a] and extractability to Ag^+ ion

Ligand	**1**	**2**	**3**	**4**	**5**	**12**
K_a	0.52	2.3×10	5.2×10^2	1.3×10^3	1.6×10^3	2.3×10^2
Extractability	2	42	51	92	93	59

[a] Determined in CD_3CN at 25 °C. Reproducibility was ±10%, which was the average value obtained from three independent runs.

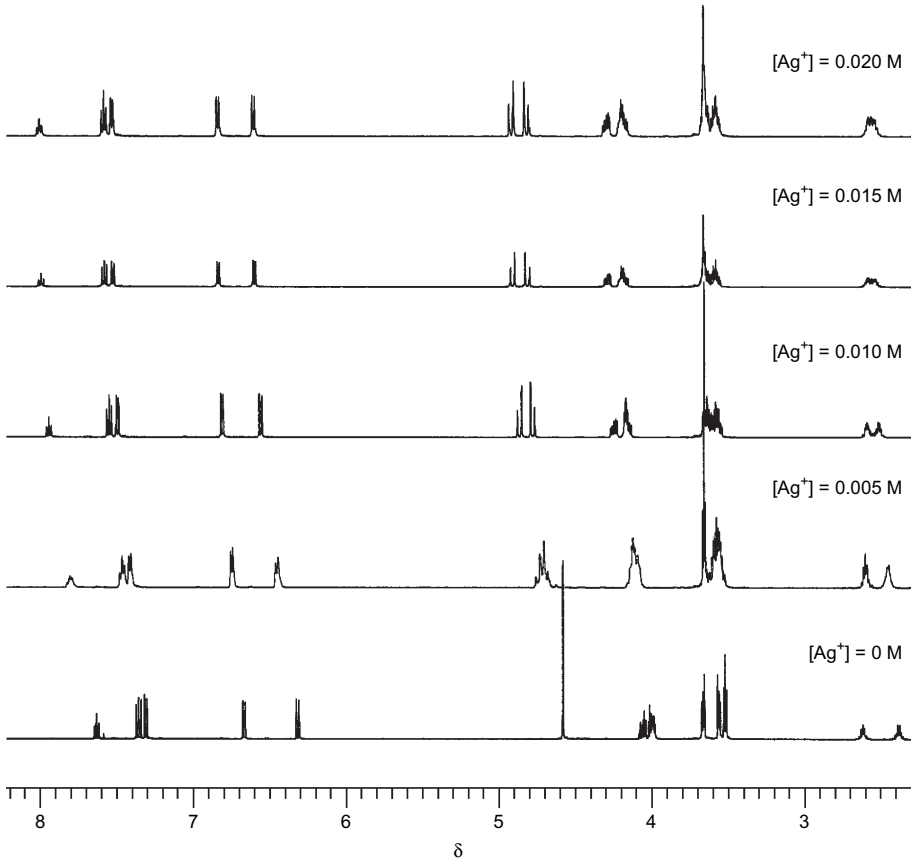


Figure 3. ^{1}H NMR spectra of **5** with $AgClO_4$ in CD_3CN. [**5**]=0.010 mol dm^{-3}.

As shown in Figure 3, for example, the ^{1}H NMR chemical shifts and the peak shapes of the aromatic and the polyether significantly changed by the addition of $AgClO_4$ up to 1:1 mole ratio to **5**. When more than equimolar salt was added, no further change was observed. It is suggested that the conformation of flexible **5** is finally fixed to a certain form, where three pyridine moieties and polyether moieties cooperatively acted as ligating sites for the cation.

To clarify the complexing behavior of **5** to Ag^+, we investigated the interaction between **5** and Ag^+ ion in CH_3CN–H_2O (1:1) by ESI-MS (Fig. 4). It was found that a 1:1 complex

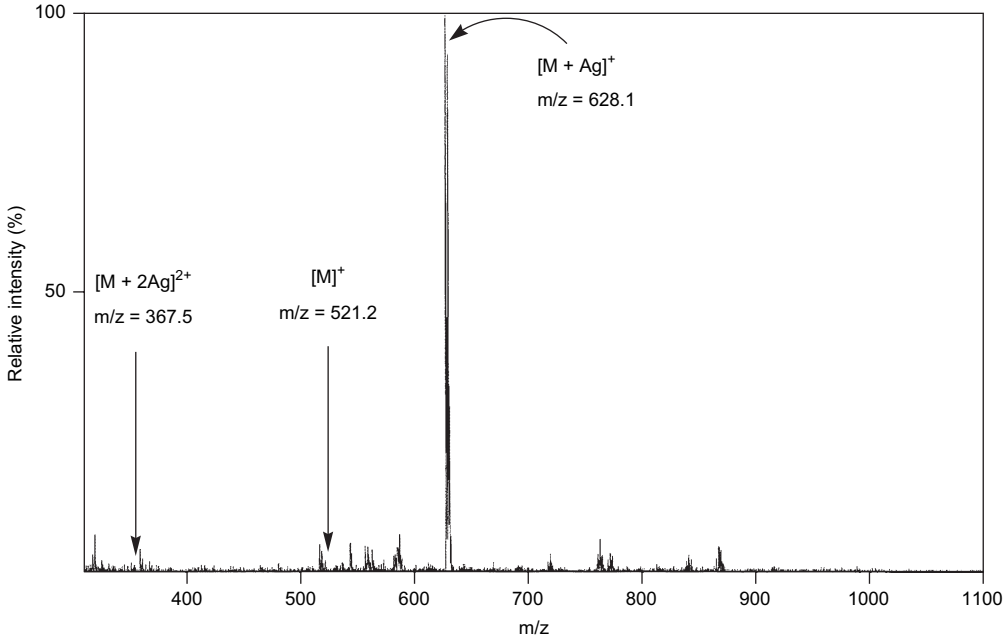


Figure 4. ESI-MS spectrum of **5** in 1:1 (v/v) CH_3CN–H_2O containing $AgClO_4$. [**5**]=[$AgClO_4$]=0.01 mmol dm^{-3} (MeCN/H_2O=4:1).

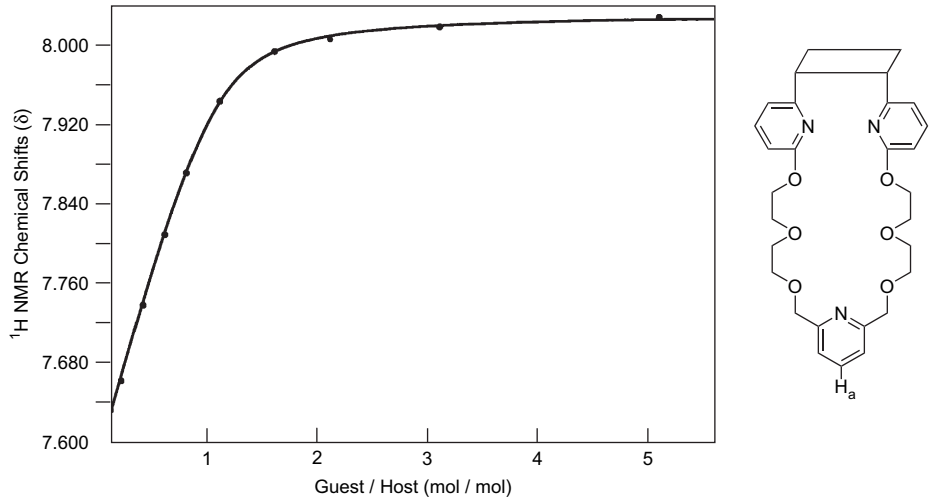


Figure 5. ^{1}H NMR titration of crownobipyridinophane **5** with $AgClO_4$. Symbols are experimental data points. A line is the best-fit curve calculated from non-linear least-squares fitting analysis in CD_3CN. H_a was monitored after each addition of $AgClO_4$. [**5**]=0.010 mol dm^{-3}.

with Ag^+ ion exclusively formed, because no peak was observed at mass number corresponded to those of free host and the other stoichiometric complexes. Pyridinophane **4** also showed the same behavior at the complexation with Ag^+ ion in the solution.

2.3. Complexing stability constant (K_a) of the pyridinocrownophanes and reference compounds

The values of percent extraction for Ag^+ ion of **4** and **5** are close to the upper limit. Thus, we measured complexing stability constant (K_a) between these phanes and Ag^+ ion in order to evaluate their complexing ability more quantitatively by a curve fitting method on the basis of the ^{1}H NMR data as shown in Figure 5.

The values of the pyridinophanes **4** and **5** are extremely high compared to not only that of the corresponding pyridinophane **3**, but also that of **2**. This indicates the cooperation of the ethereal oxygen atoms and the three nitrogen atoms in the pyridinophanes. Thus, a large effect by introducing the additional pyridine moieties in the polyether linkage on the complexation with Ag^+ ion was demonstrated at the same time.

3. Conclusion

The pyridinocrownophanes were prepared by means of intramolecular [2+2] photocycloaddition of styrene and vinylbipyridine derivatives. In the homogeneous acetonitrile solution, the pyridinocrownophanes possessing three pyridine rings showed extraordinarily high affinity toward Ag^+ ion. And also their liquid–liquid extraction showed extremely high extractability. This is rationalized by the cooperation of the ethereal ligating sites and the three nitrogen atoms in the crownophanes.

4. Experimental

4.1. Apparatus

^{1}H NMR spectra were recorded on a JEOL-500 FT NMR spectrometer (500 MHz) using tetramethylsilane as an internal standard. Elemental analysis was carried out in the Technical Research Center for Instrumental Analysis, Gunma University. 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.

4.2. Reagents

THF was purified by distillation over Na after prolonged reflux under a nitrogen atmosphere. Guaranteed reagent grade DMF was used without purification. Guaranteed reagent grade MeCN and CH_2Cl_2 were distilled before use. Reagent grade dibenzopyridino-18-crown-6 (**12**) was used without further purification. The commercially available highest grade of $AgNO_3$, $Pb(NO_3)_2$, $Cu(NO_3)_2$, $Mn(NO_3)_2$, $Zn(NO_3)_2$, $Ni(NO_3)_2$, $Co(NO_3)_2$, and $AgClO_4$ were used after drying in vacuum. All aqueous solutions were prepared with distilled, deionized water.

4.3. Synthesis of pyridinocrownophanes

4.3.1. General procedure for preparation of diethylene glycol mono(bromopyridyl) ethers (6 and 9). A THF solution (50 mL) of diethylene glycol (45.49 g, 4.29×10^{-1} mol) was added to a suspension of NaH (60% in oil, 5.02 g, 1.27×10^{-1} mol, washed with *n*-hexane by decantation) in THF (50 mL) with stirring for 10 min at room temperature. After the evolution of hydrogen gas has ceased, a DMF solution (150 mL) of dibromopyridine (10.21 g, 4.31×10^{-2} mol) was added to the suspension with stirring for 0.5 h at room temperature. Then the mixture was stirred at

reflux for 8 h at 60 °C, cooled to room temperature, and 1:4 THF aqueous solution was added to destroy excess NaH. Water (150 mL) was added and then the mixture was extracted with methylene chloride (150 mL×3). The organic solution was washed with water (300 mL×3), dried on $MgSO_4$, and evaporated in vacuo. The residue was purified by column chromatography (SiO_2, a gradient mixture of toluene and ethyl acetate) to afford the bromopyridine derivative. Compound **6**: yield 89%; mp 39.8–40.8 °C; ^{1}H NMR ($CDCl_3$) δ=8.17 (1H, d, J=2.4 Hz), 7.65 (1H, dd, J=2.4 and 8.8 Hz), 6.71 (1H, d, J=8.8 Hz), 4.48–4.45 (2H, m), 3.87–3.84 (2H, m), 3.78–3.73 (2H, m), 3.69–3.64 (2H, m). Compound **9**: yield 78%; transparent viscous liquid; ^{1}H NMR ($CDCl_3$) δ=7.41 (1H, t, J=7.8 Hz), 7.06 (1H, dd, J=0.6 and 7.4 Hz), 6.72 (1H, dd, J=0.6 and 8.2 Hz), 4.50–4.47 (2H, m), 3.86–3.82 (2H, m), 3.77–3.72 (2H, m), 3.66–3.63 (2H, m).

4.3.2. General procedure for preparation of diethylene glycol mono(vinylpyridinyl) ethers (7 and 10). A solution of the precursor bromopyridine derivative (4.00 g, 1.53×10^{-2} mol), tri-*n*-butylvinylstannane (4.76 g, 1.50×10^{-2} mol), $Pd(PPh_3)_4$ (0.59 g, 5.10×10^{-4} mol), and 2,6-di-*tert*-butyl-4-methylphenol (15 mg) in toluene (50 mL) was heated to reflux for 1.5 h. After the mixture was cooled to ambient temperature, a large excess of 2 M aqueous KF solution (28 mL) was added, and the resulting mixture was stirred for 1 h at the same temperature. The organic layer was separated from the sludge and the aqueous layers. The sludge and the aqueous layers were extracted with toluene (150 mL), and the combined organic solution was dried over $MgSO_4$. The concentrated crude material was purified by column chromatography (SiO_2, a gradient mixture of toluene and ethyl acetate) to afford the vinylpyridine derivative. Compound **7**: yield 76%; pale yellow viscous liquid; ^{1}H NMR ($CDCl_3$) δ=8.09 (1H, d, J=2.4 Hz), 7.71 (1H, dd, J=2.5 Hz and 8.6 Hz), 6.76 (1H, d, J=8.6 Hz), 6.65–6.59 (1H, m), 5.64 (1H, dd, J=0.3 and 17.6 Hz), 5.22 (1H, dd, J=0.7 and 10.9 Hz), 4.51–4.48 (2H, m), 3.88–3.86 (2H, m), 3.78–3.73 (2H, m), 3.69–3.64 (2H, m). Compound **10**: yield 75%; pale yellow viscous liquid; ^{1}H NMR ($CDCl_3$) δ=7.50 (1H, t, J=7.8 Hz), 6.81 (1H, d, J=7.2 Hz), 6.71 (1H, d, J=10.5 Hz), 6.65 (1H, d, J=8.8 Hz), 6.23 (1H, dd, J=1.8 and 17.1 Hz), 5.38 (1H, dd, J=1.8 and 10.5 Hz), 4.55–4.52 (2H, m), 3.88–3.84 (2H, m), 3.75–3.66 (2H, m), 3.65–3.63 (2H, m).

4.3.3. General procedure for preparation of α,ω-bis-(vinylpyridyl)oligooxyethylene (8 and 11). A THF solution (40 mL) of **7** or **10** (1.21 g, 5.78×10^{-3} mol) was added to a suspension of NaH (60% in oil, 0.31 g, 7.64×10^{-3} mol, washed with hexane) with stirring at ambient temperature over a period of 20 min. The reaction mixture was allowed to reflux and stirred for 1 h. After the mixture was cooled to −70 °C, 2,6-bis[(tosyloxy)methyl]pyridine (0.85 g, 1.91×10^{-3} mol) dissolved in 50 mL of THF was added dropwise in it in 0.5 h. The mixture was stirred at −70 °C for 1 h and then at ambient temperature for 24 h. A small amount of water was carefully added to destroy excess NaH. The solid material was filtered off. The filtrate was evaporated in vacuo and the residue was purified by column chromatography (SiO_2, a gradient solution of toluene and ethyl acetate) to give the target compound. Compound **8**: yield 48%; pale yellow viscous liquid; ^{1}H NMR ($CDCl_3$) δ=8.08 (2H, d, J=2.4 Hz), 7.70–7.64 (3H, m), 7.35 (2H, d, J=7.7 Hz), 7.76 (2H, d, J=8.6 Hz), 6.69–6.59 (2H, m), 5.63 (2H, dd, J=0.7 and 17.6 Hz), 5.21 (2H, dd, J=0.7 and 10.9 Hz), 4.67 (4H, s), 4.51–4.48 (4H, m), 3.89–3.86 (4H, m), 3.80–3.72 (8H, m). Compound **11**: yield 26%; pale yellow viscous liquid; ^{1}H NMR ($CDCl_3$) δ=7.58 (1H, t, J=7.6 Hz), 7.44 (2H, t, J=7.8 Hz), 7.30 (2H, d, J=7.6 Hz), 6.74 (2H, d, J=7.0 Hz), 6.61 (2H, dd, J=10.5 and 17.4 Hz), 6.59 (2H, d, J=7.9 Hz), 6.18 (2H, dd, J=1.8 and 17.4 Hz), 5.31 (2H, dd, J=1.7 and 10.5 Hz), 4.60 (4H, s), 4.48 (4H, t, J=4.9 Hz), 3.83 (4H, t, J=4.9 Hz), 3.71–3.68 (8H, m).

4.3.4. General procedure for preparation of pyridinocrownophanes (4 and 5). The photocycloaddition was carried out by a conventional method developed by us.[28] Into a 500-mL flask with a magnetic stirring and N_2 inlet was placed the precursor (**8** or **10**: 0.47 g, 9.01×10^{-4} mol) dissolved in MeCN (500 mL), and nitrogen gas was bubbled in for 40 min. The solution was irradiated by a 400-W high-pressure mercury lamp through a Pyrex filter. The reaction was monitored by HPLC and TLC. After the disappearance of the olefin (ca. 40 min), the reaction mixture was evaporated and then the crude reaction product was purified by column chromatography (SiO_2, a gradient mixture of toluene and ethyl acetate) to afford pyridinocrownophane. Compound **4**: yield 20%; mp 90.6–91.5 °C; ^{1}H NMR ($CDCl_3$) δ=7.88 (2H, s), 7.52 (2H, d, J=7.7 Hz), 7.36 (1H, t, J=7.7 Hz), 7.00 (2H, d, J=8.4 Hz), 6.55 (2H, d, J=8.4 Hz), 4.68 (4H, s), 4.40–4.35 (4H, m), 3.95–3.91 (2H, m), 3.83–3.81 (4H, m), 3.78–3.66 (8H, m), 2.50–2.45 (2H, m), 2.38–2.33 (2H, m). ^{13}C NMR ($CDCl_3$) δ=162.2, 157.9, 145.4, 138.7, 129.0, 120.1, 110.9 (2C), 73.4, 70.4, 69.8, 69.4, 65.2, 41.8, 24.0. Anal. Calcd for $C_{29}H_{35}N_3O_6$: C, 66.78; H, 6.76; N, 8.06. Found: C, 66.74; H, 6.90; N, 8.11. Compound **5**: yield 16%; mp 89.3–90.2 °C; ^{1}H NMR ($CDCl_3$) δ=7.43 (1H, t, J=8.2 Hz), 7.33–7.22 (4H, m), 6.53 (2H, dd, J=0.6 and 7.2 Hz), 6.32 (2H, dd, J=0.6 and 8.2 Hz), 4.67 (4H, s), 4.23–4.12 (4H, m), 4.03–3.86 (2H, m), 3.73–3.71 (4H, m), 3.67–3.63 (8H, m), 2.70–2.64 (2H, m), 2.41–2.36 (2H, m). ^{13}C NMR ($CDCl_3$) δ=162.4, 159.7, 137.9, 137.9, 120.9, 115.2, 108.0, 107.5, 73.7, 70.6, 69.9, 69.6, 64.7, 45.7, 23.7. Anal. Calcd for $C_{29}H_{35}N_3O_6$: C, 66.78; H, 6.76; N, 8.06. Found: C, 66.74; H, 6.77; N, 8.16.

4.4. Solvent extraction of heavy metal nitrates

A CH_2Cl_2 solution of bipyridinocrownophane (1×10^{-4} mol dm^{-3}, 5.0 mL) and an aqueous metal nitrate solution (0.1 mol dm 1^{-3}, 5.0 mL), whose pH value was adjusted as high as possible not to precipitate the hydroxides, were shaken in a 20-mL test tube with a ground-glass stopper at an ambient temperature (ca. 20 °C) for 1.5 h. Two liquid phases were separated and evaporated in vacuo. The residue was dissolved in 0.1 mol dm^{-3} HNO_3 for analysis by atomic absorption spectrometry.

4.5. ESI-MS measurement of bipyridinocrownophane in the presence of silver perchlorate

The sample solution ($MeCN/H_2O$ [4:1 (v/v)]) contained crownobipyridinophane (0.01 mmol dm^{-3}) and the metal salt (0.01 mmol dm^{-3}).

4.6. ^{1}H NMR titration of the pyridinocrownophane with silver perchlorate

A solution of the phanes (0.01 mol dm^{-3}) was prepared, and its 500 μL portion was placed in an NMR tube, and the solvent level was marked. A second solution was made in acetonitrile-d_3 with the metal nitrate. 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 10 equiv to the crownophane. The chemical shifts of the aromatic proton of the phanes before and after each addition of the guest solution were used for calculation of the association constants (K_a). The constants were determined by nonlinear least-squares fitting method of the titration curves for 1:1 complexation, which was monitored by the ESI-MS analysis.

References and notes

1. Weber, E.; Vögtle, F. *Angew. Chem.* **1980**, *92*, 1067–1068.
2. Buhleier, E.; Frensch, K.; Luppertz, F.; Vögtle, F. *Justus Liebigs Ann. Chem.* **1978**, 1586–1591.
3. Frensch, K.; Vögtle, F. *Tetrahedron Lett.* **1977**, 2573–2574.
4. Weber, E.; Vögtle, F. *Chem. Ber.* **1976**, *109*, 1803–1831.
5. Newkome, G. R.; Charles, R. *Tetrahedron* **1983**, *39*, 2001–2008.
6. Fronczek, F. R.; Majestic, V. K.; Newkome, G. R.; William, E.; Atwood, J. L. *J. Chem. Soc., Perkin Trans. 2* **1981**, 331–335.
7. Newkome, G. R.; Danesh-Khoshboo, F.; Najak, A.; William, H. *J. Org. Chem.* **1978**, *43*, 2685–2690.
8. Newkome, G. R.; Kawato, T. *J. Org. Chem.* **1979**, *44*, 2693–2697.
9. Newkome, G. R.; Kawato, T.; Najak, A. *J. Org. Chem.* **1979**, *44*, 2697–2702.
10. Zolgharnein, J.; Tahmasebi, H.; Habibi, M.; Amani, S. *J. Inclusion Phenom.* **2004**, *49*, 231–234.
11. Vetrichelvan, M.; Lai, Y.-H.; Mok, K. F. *Eur. J. Inorg. Chem.* **2004**, 2086–2095.
12. Takemura, H.; Kon, N.; Yasutake, M.; Shinmyozu, T. *Tetrahedron* **2003**, *59*, 427–431.
13. Fenton, R. R.; Gauci, R.; Junk, P. C.; Lindoy, L. F.; Luckey, R. C.; Meehan, G. V.; Price, J. R.; Turner, P.; Wei, G. *J. Chem. Soc., Dalton Trans.* **2002**, 2185–2193.
14. Yamato, T.; Zhang, F.; Kumamura, K.; Yamamoto, H. *J. Inclusion Phenom.* **2002**, *42*, 51–60.
15. Kumar, S.; Kaur, S.; Singh, H. *J. Inclusion Phenom.* **2001**, *39*, 277–283.
16. Adams, H.; Elsegood, M. R. J.; Fenton, D. E.; Heath, S. L.; Ryan, S. J. *J. Chem. Soc., Dalton Trans.* **1999**, 2013–2038.
17. Kumar, S.; Bhalla, V.; Singh, H. *Tetrahedron* **1998**, *54*, 5575–5586.
18. Kumar, S.; Hundal, M. S.; Hundal, G.; Kaur, N.; Singh, H. *Tetrahedron* **1997**, *53*, 10481–10850.
19. Nabeshima, T.; Aoki, T.; Yano, Y. *Tetrahedron Lett.* **1997**, *38*, 8323–8326.
20. Kumar, S.; Hundal, M. S.; Hundal, G.; Kaur, N.; Singh, R.; Singh, H.; Sood, G. H.; Ripoll, M. M.; Aparicio, J. S. *J. Org. Chem.* **1996**, *61*, 7819–7825.
21. Adams, H.; Bailey, N. A.; Fenton, D. E.; Ho, Y.-S. *Inorg. Chim. Acta* **1993**, *212*, 65–68.
22. Tsukube, H.; Uenishi, J.; Higaki, H.; Kikkawa, K.; Tanaka, T.; Wakabayashi, S.; Oae, S. *J. Org. Chem.* **1993**, *58*, 4389–4397.
23. Tsukube, H.; Minatogawa, H.; Munakata, M.; Toda, M.; Matsumoto, K. *J. Org. Chem.* **1992**, *57*, 542–547.
24. Adams, H.; Bailey, N. A.; Carlisle, W. D.; Fenton, D. E.; Rossi, G. *J. Chem. Soc., Dalton Trans.* **1990**, 1271–1283.
25. Inokuma, S.; Sakai, S.; Katoh, R.; Nishimura, J. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1462–1467.
26. Inokuma, S.; Yasuda, T.; Araki, S.; Sakai, S.; Nishimura, J. *Chem. Lett.* **1994**, 201–204.
27. Inokuma, S.; Kimura, K.; Funaki, T.; Nishimura, J. *Heterocycles* **2001**, *55*, 447–451.
28. Inokuma, S.; Yamamoto, T.; Nishimura. *Tetrahedron Lett.* **1990**, *31*, 97–100.
29. Inokuma, S.; Kimura, K.; Funaki, T.; Nishimura, J. *Heterocycles* **2001**, *54*, 123–130.
30. Inokuma, S.; Ide, H.; Yonekura, T.; Funaki, T.; Kondo, S.; Shiobara, S.; Yoshihara, T.; Tobita, S.; Nishimura, J. *J. Org. Chem.* **2005**, *70*, 1698–1703.
31. McKean, D. R.; Parrinello, G.; Renaldo, A. F.; Stille, J. K. *J. Org. Chem.* **1987**, *52*, 422–424.
32. Nishimura, J.; Ohbayashi, A.; Doi, H.; Nishimura, K.; Oku, A. *Chem. Ber.* **1988**, *121*, 2019–2024.
33. Inokuma, S.; Nishimura, J. Unpublished.