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Tetrahedron
Tetrahedron 62 (2006) 10005–10010

Synthesis of crownophanes possessing bipyridine moieties: bipyridinocrownophanes exhibiting perfect extractability toward Ag^+ ion

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Received 29 November 2005; revised 1 August 2006; accepted 1 August 2006
Available online 1 September 2006

Abstract—Novel crownophanes with two bipyridine moieties (bipyridinocrownophanes **1a** and **1b**) were conveniently prepared by means of intramolecular [2+2] photocycloaddition of vinylbipyridine derivatives. In the liquid–liquid extraction of heavy metal cations, **1a** and **1b** exhibited perfect selectivity toward Ag^+ with high efficiency. It was found that the ethereal oxygen atoms and the four nitrogen atoms in **1a** and **1b** acted as ligating sites, according to the high extractability and complexing stability constant for Ag^+ compared to those of the corresponding pyridinocrownophanes **4a** and **4b**. ^1H NMR and ESI-MS analyses suggested that the crownophanes formed a 1:1 complexes with the Ag^+ ion.

1. Introduction

The pyridine moiety is known to act as a good ligating site for the Ag^+ ion when it is arranged at a suitable position in a host molecule.[1–9] We have prepared some pyridinophanes[10] and crownophanes possessing pyridine moieties as side ligating groups.[11–13] They were directly prepared by intramolecular [2+2] photocycloaddition of styrene derivatives or indirectly by modification to dihydroxycrownophanes.[14] Recently, we have synthesized crownopyridinophanes by the above photocycloaddition of vinylpyridine derivatives[16] and clarified their exclusive selectivity toward the Ag^+ cation with moderate efficiency.[17] It is considered that the extraordinarily high Ag^+ affinity could be achieved by an additional introduction of pyridine moieties into the pyridinocrownophanes, since bipyridine residues have been found to act as ligating parts for complexation with some metal cations including silver[18] and lantanide cations.[19–22] Hence, we were prompted to synthesize crownophanes possessing bipyridine moieties (bipyridinocrownophanes). The structural analysis and complexing ability of the bipyridinophanes are also described in this paper.

2. Results and discussion

2.1. Synthesis of bipyridinocrownophanes

Bipyridinocrownophanes, **1a** and **1b**, were prepared by the method shown in Scheme 1. Compounds **2a** and **2b** were easily obtained from the reaction of 6,6′-dibromo-2,2′-bipyridine with oligo(ethyleneglycol) in moderate yield. Precursor olefins **3a** and **3b** were prepared by Stille reaction[23] in excellent yield. The target crownophanes **1a** and **1b** were synthesized by photocycloaddition.[14]

From the ^1H NMR analysis **1a** and **1b** were found to have a 1,2-substituted *cis*-cyclobutane ring, which was proved by the specific methine proton signals at δ 4.31 and 4.29 (in $CDCl_3$),[15] respectively. As shown in Figure 1, all the aromatic proton peaks were high-field shifted compared to those of the aromatic nuclei, indicating the phane structure.

2.2. Crystal structure of crownobipyridinophane 1a

Single crystals of **1a** were obtained from methanol–CH_2Cl_2 solution. As illustrated in Figure 2, the solid-state structure of free ligand **1a** is not thought to be suitable to accommodate a certain cation from the following aspects: (1) The cyclobutane ring (C21–C24) is tilted toward the nitrogen atoms (N1 and N3) of the proximal pyridine rings. This suggests that the cyclobutane ring can prevent any species from ligating to the nitrogen sites. (2) Nitrogen atoms (N2 and N4) of

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Keywords: Crown compound; Cyclophane; Extraction; Ag^+-selective ionophore; [2+2] Photocycloaddition.

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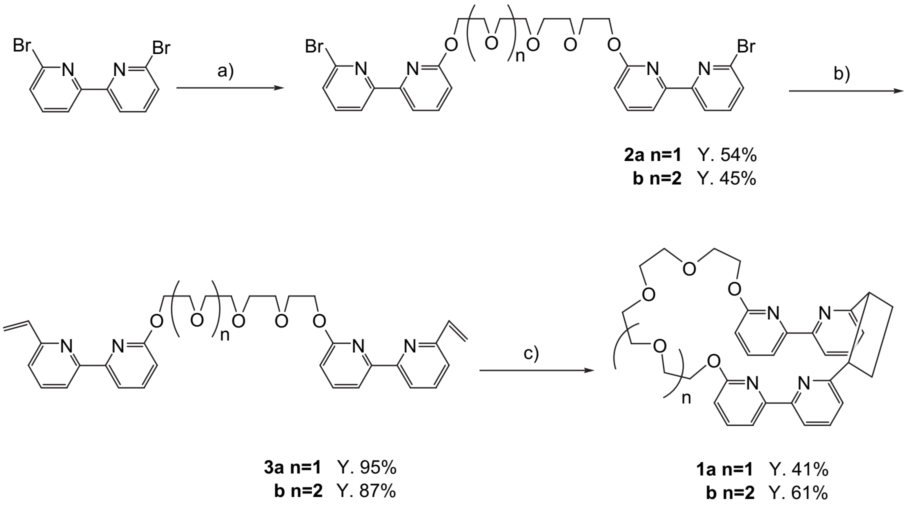
doi:10.1016/j.tet.2006.08.005



Scheme 1. Synthesis of bipyridinocrownophanes **1a** and **1b**. Reagents and conditions: (a) $HO(C_2H_4O)_{n+3}H$, NaH–THF; (b) $CH_2{=}CHSn(n\text{-}Bu)_3$, $Pd(PPh_3)_4$, 2,6-di-*tert*-butyl-4-methylphenol–toluene; (c) hν (>280 nm)/MeCN.

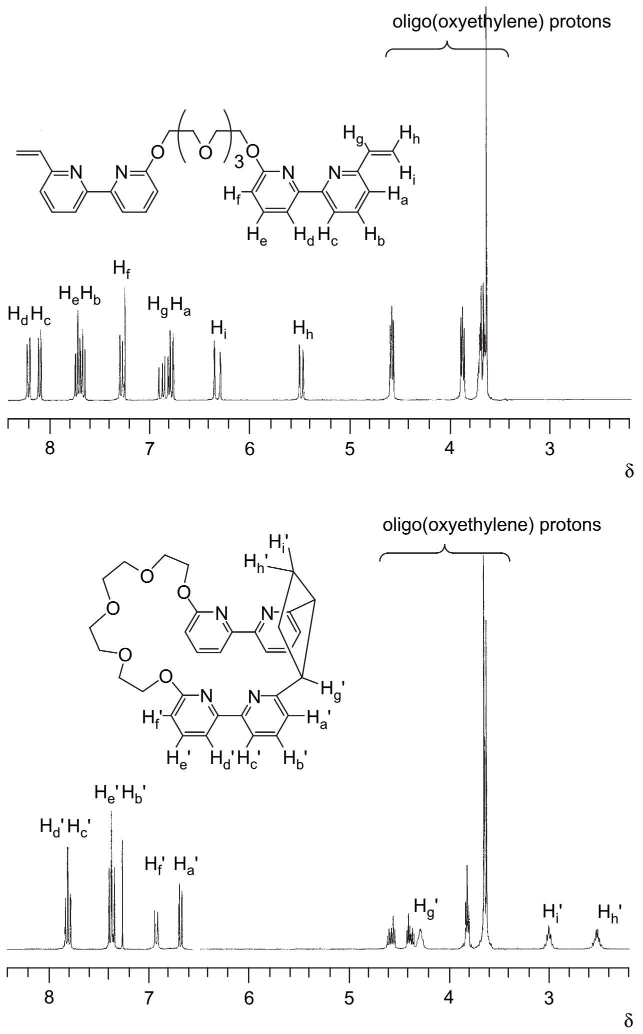


Figure 1. ^1H NMR spectra of precursor olefin **3a** and bipyridinocrownophane **1a** within $CDCl_3$.

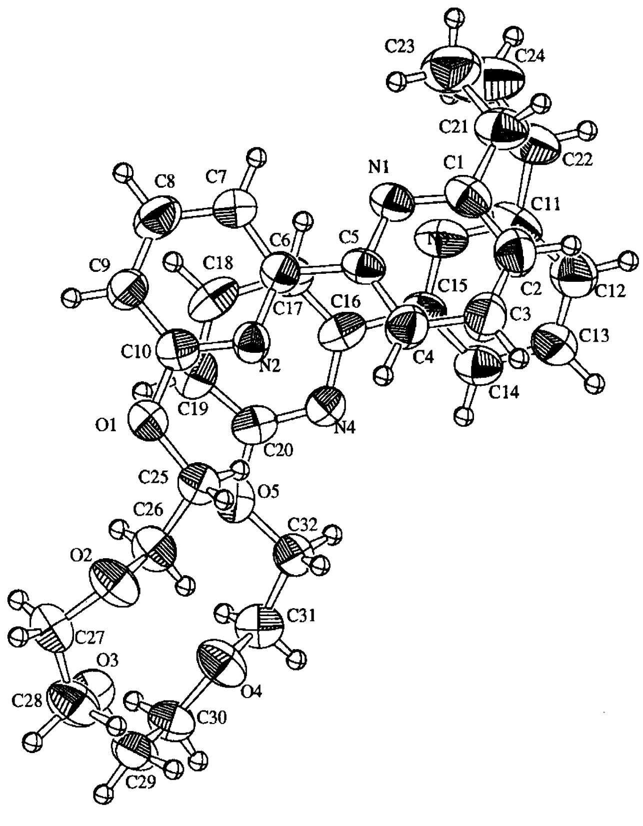


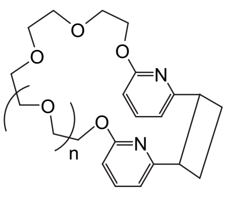
Figure 2. ORTEP drawing of **1a**.

the distal pyridine rings possessing a polyether linkage from the cyclobutane ring are arranged in the opposite direction against the proximal pyridine rings, indicating that all the ligating sites do not act cooperatively. To confirm whether the unfavorable situation for cooperative complexation is retained or not in the solution, we tried liquid–liquid extraction by using the phanes as extraction reagents as will be mentioned in the following section.

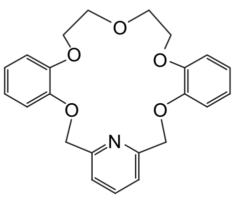
2.3. Complexing behavior of bipyridinocrownophanes toward heavy metal cations

Liquid–liquid extraction of heavy metal cations by bipyridinocrownophanes was carried out with pyridinocrownophanes **4a** and **4b** and dibenzopyridino-18-crown-6 **5** as

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



4a n=1
b n=2



5

Ligand	Extractability (%)[a]						
	Ag^+	Pb^{2+}	Cu^{2+}	Mn^{2+}	Zn^{2+}	Ni^{2+}	Co^{2+}
1a	90(6.0)	0(4.5)	1(4.3)	0(6.7)	0(6.1)	0(6.7)	0(7.1)
1b	93(6.3)	0(4.5)	4(4.5)	0(6.7)	1(6.3)	2(6.8)	0(7.1)
4a	42(4.2)	0(5.2)	0(4.5)	0(6.8)	0(7.2)	0(6.2)	0(7.2)
4b	23(5.2)	0(4.7)	0(4.4)	0(5.3)	0(5.9)	0(5.7)	0(6.4)
5	59(5.5)	10(5.6)	0(4.2)	0(6.3)	2(6.2)	0(6.7)	0(6.9)

[a] Extraction conditions: aq phase (5 mL), [metal nitrate]=1.0×10^{-1} mol dm^{-3}; org. phase, CH_2Cl_2 (5 mL), [ligand]=1.0×10^{-4} mol dm^{-3}, at ca. 20 °C, shaken for 1.5 h. The values were based on the concentration of the crown compounds. Values in parentheses were equilibrium pH of aqueous phase. Reproducibility was ±15%, which was the average value obtained from three independent runs.

reference compounds. Although **5** extracted a Pb^{2+} ion other than the Ag^+ ion, bipyridinocrownophanes **1** exclusively extracted the Ag^+ ion with high efficiency among the heavy metal cations tested. The remarkably high efficiency of **1** compared to that of **4** means the contribution of additional pyridine rings of **1** for Ag^+-complexation. Of course, it indicates that the ethereal oxygen atoms and the four nitrogen atoms in the pyridine ring acted as effective ligating sites cooperatively similar to that of **4**[17] (Table 1).

As shown in Figure 3, the ^1H NMR chemical shifts and the peak shapes of the aromatic and the polyether protons significantly changed during the increase of the amount to equimolar $AgClO_4$ added to **1**. When more than equimolar of the salt was ([Ag^+]=0.025 M) added, no change was observed. It is suggested that the conformation of **1** is finally fixed to a certain form, where bipyridine moieties and polyether moieties cooperatively acted as ligating sites for the cation.

Namely, the donating sites of all the four nitrogen atoms and the ethereal oxygen atoms are thought to converge to form a highly stable complex in the solubilized conditions.

The efficiency of **4a** and **4b** remarkably differs from each other, while the higher efficiency of **1a** and **1b** than those of **4a** and **4b** is almost the same, suggesting that their complexing stability constants are nearly the same.

2.4. ESI-MS analysis of bipyridinocrownophane–Ag^+ complex

To clarify the complexing behavior of **1** to Ag^+, we investigated the interaction between **1a** and the Ag^+ ion in CH_3CN–H_2O (1:1) by ESI-MS (Fig. 4). It was found that a 1:1 (host–guest) complex with the Ag^+ ion exclusively formed, because no peak was observed at the mass number corresponding to those of the free host and the other stoichiometric

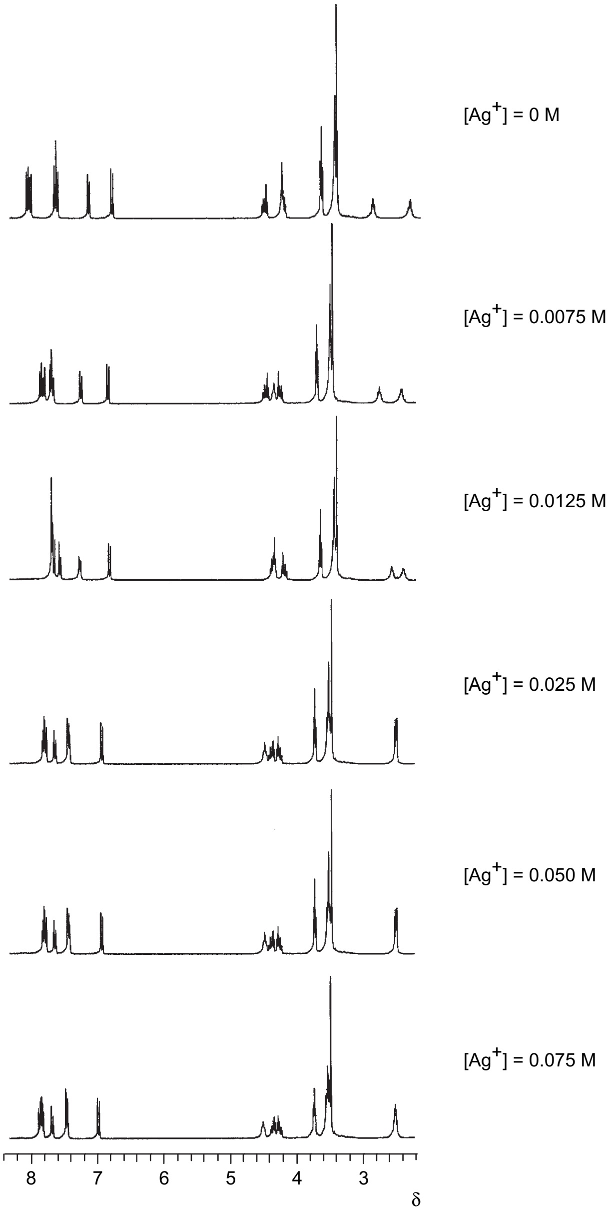


Figure 3. ^1H NMR spectra of **1a** with $AgClO_4$ in CD_3CN. [**1a**]=0.025 M.

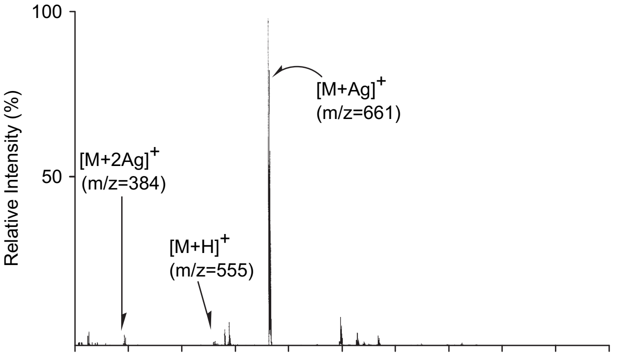


Figure 4. ESI-MS spectrum of **1a** in 1:1 (v/v) CH_3CN–H_2O containing $AgClO_4$. [**1a**]=[$AgClO_4$]=0.1 mM (MeCN–H_2O=4:1).

complexes. Phane **1b** also showed the same behavior at the complexation with the Ag^+ ion in the solution.

2.5. Complexing stability constant (K_a) of bipyridinocrownophanes and reference compounds

As mentioned in the section of the liquid–liquid extraction, the values of percent extraction for the Ag^+ ion of **1a** and **1b** are close to the upper limit. Thus, we measured complexing stability constant (K_a) between these phanes and the Ag^+ ion in order to evaluate their complexing ability more quantitatively by nonlinear least-squares fitting method for the ^1H NMR titration curve (shown in Fig. 5, for example).

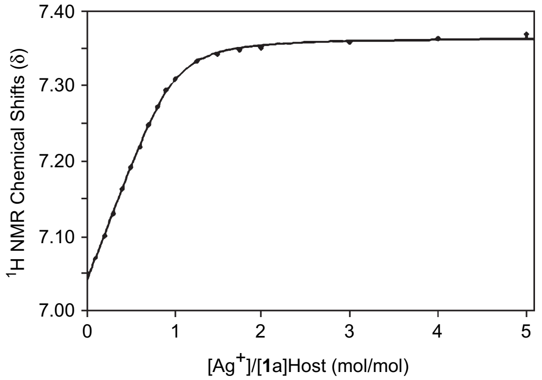
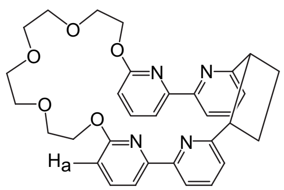


Figure 5. ^1H NMR titration of crownobipyridinophane **1a** with $AgClO_4$ in CD_3CN. [**1a**]=10 mM. H_a was monitored after each addition of $AgClO_4$.



1a

The values of the bipyridinophanes **1a** and **1b** are extremely high compared to not only those of the corresponding pyridinophanes **4a** and **4b**, but also that of **5**. This indicates the cooperation of the ethereal oxygen atoms and the four nitrogen atoms in the bipyridinophanes, which is in agreement with the results of ^1H NMR study in the presence of the Ag^+ ion shown in Figure 3. Thus, a large effect by introducing the additional pyridine moieties in the pyridinophanes on the complexation with the Ag^+ ion was demonstrated at the same time. Furthermore, large different K_a was confirmed between **1a** and **1b** suggesting that longer ethereal linkage was necessary to more effectively bind to the cation by cooperative action between all four pyridine nitrogen atoms and the ethereal oxygen atoms, though little different K_a was observed between the corresponding pyridinophanes **4a** and **4b** with only two pyridine moieties (Table 2).

Table 2. Stability constant (K_a) of the pyridinophanes and reference compound[a]

Ligand	**1a**	**1b**	**4a**	**4b**	**5**
K_a	2.56×10^3	3.25×10^4	27	22	231

[a] Determined in acetonitrile-d_3 at 25 °C.

3. Conclusion

The bipyridinocrownophanes were conveniently prepared by means of intramolecular [2+2] photocycloaddition of vinylbipyridine derivatives. In the liquid–liquid extraction and the homogeneous acetonitrile solution, the bipyridinocrownophanes showed extraordinarily high affinity toward the Ag^+ ion. This is caused by the cooperation of the ethereal ligating sites and the four nitrogen atoms in the crownophanes.

4. Experimental

4.1. Apparatus

^1H NMR and ^{13}C 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. Mass spectra (HRMS) were determined by a JEOL JSM-BU25. 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 (**5**) 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 bipyridinocrownophanes

4.3.1. Preparation of α,ω-bis(6-bromo-2,2′-bipyridil)-oligo(oxyethylene) 2. Oligo(ethyleneglycol) (15.9 mmol) was added to a suspension of NaH (60% in oil, 0.15 g, 3.82 mmol, washed with *n*-hexane by decantation) in THF (8 mL) at room temperature. After the evolution of hydrogen gas ceased, a THF (20 mL) solution of 6,6′-dibromo-2,2′-bipyridine (2.00 g, 6.36 mmol) was added to the suspension with stirring for 0.5 h at room temperature. Then the mixture was stirred at reflux for 18 h, cooled to room temperature, and 1:1 ethanol solution of hydrochloric acid was added to neutralize excess NaH. The filtered organic solution was 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 **2**. Compound **2a**: yield, 53%. White solid. Mp 69–70 °C (a mixed solvent of MeOH and CH_2Cl_2). ^1H NMR ($CDCl_3$) $\delta=8.28$ (2H, d, $J=7.6$ Hz), 8.00 (2H, d, $J=7.5$ Hz), 7.68 (2H, dd, $J=8.2$ and 7.5 Hz), 7.61 (2H, dd, $J=7.9$ and 7.6 Hz), 7.44 (2H, d, $J=7.9$ Hz), 6.82 (2H, d, $J=8.2$ Hz), 4.58 (4H, t, *J*=4.9 Hz), 3.90 (4H, t, *J*=4.9 Hz), 3.75–3.69 (8H, m). HRMS (EI): calcd for $C_{28}H_{28}Br_2N_4O_5$ (M^+) 658.0426; found 658.0410. Compound **2b**: yield, 46%. Transparent viscous liquid. ^{1}H NMR ($CDCl_3$) δ=8.29 (2H, d, *J*=7.6 Hz), 8.00 (2H, d, *J*=7.6 Hz), 7.68 (2H, dd, *J*=7.6 and 8.2 Hz), 7.64 (2H, dd, *J*=7.6 and 7.9 Hz), 7.44 (2H, d, *J*=7.9 Hz), 6.82 (2H, d, *J*=8.2 Hz), 4.58 (4H, t, *J*=4.9 Hz), 3.89 (4H, t, *J*=4.9 Hz), 3.74–3.66 (12H, m). HRMS (EI): calcd for $C_{30}H_{32}Br_2N_4O_6$ (M^+) 702.0688; found 702.0687.

4.3.2. Preparation of α,ω-bis(6-vinyl-2,2′-bipyridil)-oligo(oxyethylene) 3. A solution of **2** (7.57×10^{-1} mmol), tri-*n*-butylvinylstannane (0.58 g, 1.82 mmol), $Pd(PPh_3)_4$ (0.058 g, 5.05×10^{-2} mmol), and 2,6-di-*tert*-butyl-4-methylphenol (10 mg) in toluene (10 mL) was heated to reflux for 2 h. After the mixture was cooled to ambient temperature, a large excess of 2 M aqueous KF solution was added, and the resulting mixture was stirred overnight at the same temperature. The organic layer was separated from the sludge and aqueous layers, and then 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 vinyl compound (**3**). Compound **3a**: yield, 95%. Transparent viscous liquid. ^{1}H NMR ($CDCl_3$) δ=8.22 (2H, d, *J*=7.8 Hz), 8.11 (2H, d, *J*=7.6 Hz), 7.73 (2H, dd, *J*=7.6 and 8.1 Hz), 7.69 (2H, dd, *J*=7.8 and 7.7 Hz), 7.30 (2H, d, *J*=7.7 Hz), 6.88 (2H, dd, *J*=17.4 and 10.7 Hz), 6.80 (2H, d, *J*=8.1 Hz), 6.34 (2H, dd, *J*=17.4 and 1.2 Hz), 5.51 (2H, dd, *J*=10.7 and 1.2 Hz), 4.61 (4H, t, *J*=4.9 Hz), 3.91 (4H, t, *J*=4.9 Hz), 3.70–3.65 (8H, m). HRMS (EI): calcd for $C_{32}H_{34}N_4O_5$ (M^+) 554.2529; found 554.2531. Compound **3b**: yield, 84%. Transparent viscous liquid. ^{1}H NMR ($CDCl_3$) δ=8.22 (2H, d, *J*=7.9 Hz), 8.11 (2H, d, *J*=7.6 Hz), 7.74 (2H, dd, *J*=7.6 and 8.0 Hz), 7.69 (2H, dd, *J*=7.6 and 7.9 Hz), 7.30 (2H, d, *J*=7.6 Hz), 6.88 (2H, dd, *J*=10.7 and 17.4 Hz), 6.80 (2H, d, *J*=8.0 Hz), 6.36 (2H, dd, *J*=17.4 and 1.2 Hz), 5.52 (2H, dd, *J*=10.7 and 1.2 Hz), 4.61 (4H, t, *J*=4.9 Hz), 3.91 (4H, t, *J*=4.9 Hz), 3.74–3.67 (12H, m). HRMS (EI): calcd for $C_{34}H_{38}N_4O_6$ (M^+) 598.2791; found 598.2795.

4.3.3. Preparation of bipyridinocrownophane 1. The photocycloaddition was carried out by a conventional method developed by us.[11] Into a 300-mL flask with a magnetic stirrer and N_2 inlet was placed 2.17×10^{-1} mmol of olefin (**3**) dissolved in toluene (260 mL), and nitrogen gas was bubbled in for 20 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. 12 h), 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 **1**. Compound **1a**: yield, 41%. White solid. Mp 120–121 °C (a mixed solvent of MeOH–CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ=7.77 (2H, d, *J*=7.3 Hz), 7.72 (2H, d, *J*=7.0 Hz), 7.34 (2H, dd, *J*=7.3 and 7.3 Hz), 7.33 (2H, dd, *J*=7.0 and 7.9 Hz), 6.90 (2H, d, *J*=7.3 Hz), 6.67 (2H, d, *J*=7.9 Hz), 4.60–4.56 (2H, m), 4.36–4.31 (2H, m), 4.30–4.27 (2H, m), 3.85–3.79 (4H, m), 3.67–3.60 (8H, m), 3.06–3.03 (2H, m), 2.55–2.50 (2H, m). ^{13}C NMR ($CDCl_3$) δ=162.4, 160.2, 154.2, 153.5, 138.8, 135.7, 122.1, 117.1, 113.8, 110.5, 70.5, 70.3, 69.4, 64.6, 46.3, 22.3. HRMS (EI): calcd for $C_{32}H_{34}N_4O_5$ (M^+) 554.2529; found 554.2519. IR (KBr disk, cm^{-1}) 3050, 2953, 2872, 1572, 1436, 1337, 1326, 1274, 1148, 1114, 1065, 989, 968, 947, 907, 804, 755, 742, 632. Anal. Calcd for $C_{32}H_{34}N_4O_5$: C, 69.30; H, 6.18; N, 10.10. Found: C, 69.52; H, 6.29; N, 10.04. Compound **1b**: yield, 62%. Pale yellow solid. Mp 34–35 °C (a mixed solvent of MeOH–CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ=7.82 (2H, d, *J*=7.3 Hz), 7.80 (2H, d, *J*=8.0 Hz), 7.38 (2H, d, *J*=7.7 Hz), 7.36 (2H, d, *J*=7.9 Hz), 6.93 (2H, d, *J*=7.6 Hz), 6.68 (2H, d, *J*=8.2 Hz), 4.60–4.56 (2H, m), 4.41–4.37 (2H, m), 4.31–4.28 (2H, m), 3.85–3.80 (4H, m), 3.67–3.63 (12H, m), 3.02–3.00 (2H, m), 2.85–2.53 (2H, m). ^{13}C NMR ($CDCl_3$) δ=162.4, 160.3, 154.1, 153.4, 138.8, 135.7, 122.2, 117.1, 113.8, 110.6, 70.5 (2C), 70.3, 69.4, 64.5, 46.1, 22.7. HRMS (EI): calcd for $C_{34}H_{38}N_4O_6$ (M^+) 598.2791; found 598.2793. IR (neat, cm^{-1}) 3055, 2913, 2883, 1713, 1576, 1438, 1329, 1266, 1145, 1117, 1071, 1050, 987, 802, 751.

4.4. Crystallographic structural determination of 1a

Bipyridinocrownophane **1a** (5.0 mg) was dissolved in a mixed solvent of MeOH–CH_2Cl_2 (2 mL) under nitrogen. By slow evaporation of the solvent under nitrogen, crystallization yielded white prismatic crystals of **1a**. X-ray crystallographic data were obtained on a Rigaku AFC7S instrument. The structure was solved by direct method and expanded using Fourier techniques (DIRDIF-94 program system).

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 244232. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

4.5. Solvent extraction of heavy metal nitrates

A CH_2Cl_2 solution of bipyridinocrownophane (1×10^{-4} mol dm^{-3}, 5 mL) and an aqueous metal nitrate solution (0.1 mol dm^{-3}, 5 mL), whose pH value was adjusted as high as possible so as not to precipitate the hydroxides, were shaken in a 20-mL test tube with a ground-glass stopper at 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.

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

The sample solution (MeCN–H_2O [4:1 (v/v)]) contained a crownobipyridinophane (0.1 mM) and the metal salt (0.1 mM).

4.7. ^{1}H NMR titration of bipyridinocrownophane with silver perchlorate

A solution of the phanes (10 mmol 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 reached 10 equiv of 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.

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