Synthesis and Complexing Properties of [2.*n*](2,6)Pyridinocrownophanes

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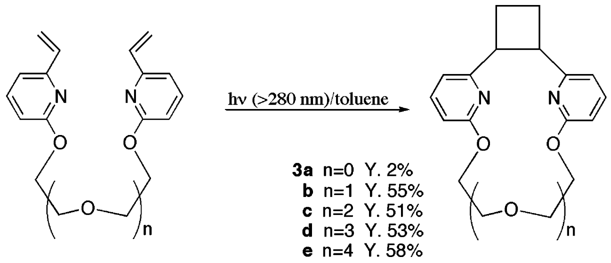

[2.*n*](2,6)Pyridinocrownophanes (**3a**−**e**) were efficiently prepared by intramolecular [2 + 2] photocycloaddition of vinylpyridine derivatives under irradiation using a 400-W high-pressure mercury lamp through a Pyrex filter. They were of *cis*-configuration with respect to the cyclobutane ring, which was proven by the specific methine proton NMR resonances at δ 3.98−4.08. From ESI-MS analysis **3a**−**e** were found to form 1:1 complexes with Ag^+ cation. In a liquid−liquid extraction, **3** showed the highest affinity toward Ag^+ cation among several heavy metal nitrates. In this series, **3c** possessing four ethereal oxygen atoms was found to show the highest Ag^+ affinity, according to the liquid−liquid extraction and determination of stability constant with the cation. The photoreactivity of precursor vinylpyridines is discussed by the predictor $\gamma(r_c)$ proposed by Caldwell.

Introduction

Pyridinophanes have attracted much interest from the structural and functional points of view. Those possessing crown ether moiety were extensively investigated by Vögtle[1−4] and Newkome[5−9] as host molecules. Other [2.2](2,5)pyridinophanes[10−12] and [3.3](2,5)- and (2,6)-pyridinophanes[13] were prepared for the structural investigation. A dynamic process of ring flipping between syn- and anti-isomers was examined with using a rather large ring system of 1,4,11,13-tetraoxa[4.4](2,6)pyridinophane.[14]

We have been extensively examining the synthesis of intramolecular [2 + 2] photocycloaddition of styrene derivatives.[15] Until recently, however, we have never succeeded in the cycloaddition of vinylpyridines by direct irradiation, although their photodimerization with sensitizer has been reported.[16] But when examined the intramolecular photocycloaddition of alkoxyvinylpyridines, we for the first time found that they produced pyridinophanes or intramolecular dimers readily by direct irradiation.[17]

In this paper, we describe the first synthesis and complexing ability of 1,2-ethano[2.*n*](2,6)pyridinophanes

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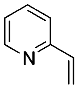
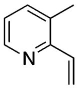
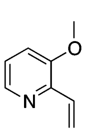
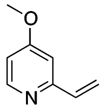
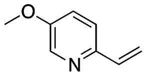
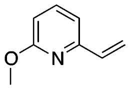
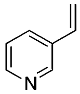
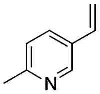
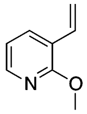
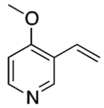
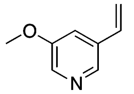
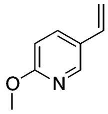
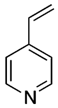
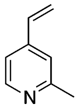
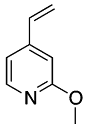
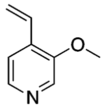
10.1021/jo0402374 CCC: $30.25

TABLE 1. Most Stable Structure of Vinylpyridine Derivatives Calculated at the PM3 Level

	Type-1	Type-2	Type-3	Type-4	Type-5	Type-6
2-Vinylpyridine						
3-Vinylpyridine						
4-Vinylpyridine						

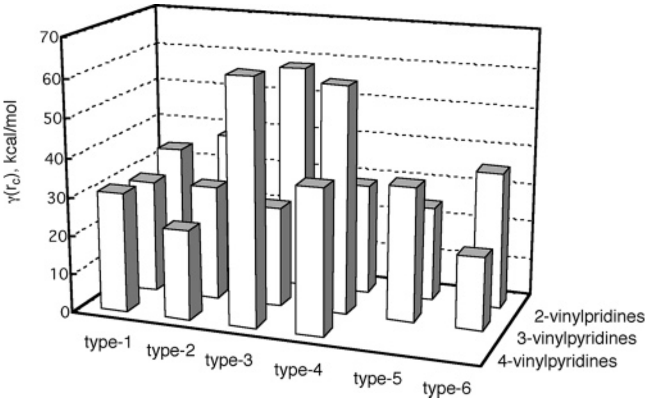


FIGURE 1. Prediction by means of Caldwell's $\gamma(r_c)$ for several vinylpyridines listed in Table 1.

possessing oligo(oxyethylene) linkages as well as the discussion on the reason the [2 + 2] photocycloaddition takes place by means of $\gamma(r_c)$ values[18] calculated for several vinylpyridine derivatives related.

Results and Discussion

Prediction Using Caldwell's $\gamma(r_c)$ for the [2 + 2] Photocycloaddition of Some Vinylpyridines. For some vinylpyridines listed in Table 1, Caldwell's $\gamma(r_c)$ values[18] were calculated with the estimation of E_S and E_T [see the Experimental Section and Table S1 (Supporting Information)]. The data are summarized in Figure 1.

Caldwell proposed that if the index $\gamma(r_c)$ for some [2 + 2] and [4 + 4] photocycloadditions under the direct irradiation or without sensitizers is less than 25 kcal/mol, the reactions would have a good chance to proceed.[18] Actually, styrene has a value of 12.1 kcal/mol and has been proven to dimerize smoothly.[19] Therefore, among vinylpyridines calculated, 2-methoxy-5-vinylpyridine (type-6 of 3-vinylpyridine in Table 1) having $\gamma(r_c)$ of 18.7 kcal/mol is expected to easily undergo the [2 + 2] photocycloaddition toward photodimers or pyridinophanes when it combines into the intramolecular system to make the reaction efficient. In fact the [2.*n*](2,5)pyridinophanes from the precursors classified as type-6 of 3-vinylpyridine in Table 1 have been successfully made and reported already.[17] As a candidate having rather large $\gamma(r_c)$ value of 35.2 kcal/mol, 2-methoxy-6-vinylpyridine derivatives **2** (type-6 of 2-vinylpyridine in Table 1) was selected and examined whether it undergoes the photoreaction or not. As mentioned below, **2** also gave desired photoadducts. This result seems to lead the violation of Caldwell's prediction, but **2a** recorded very meager yield (see Scheme 1). Since the kind of vinylpyridine is not apt to polymerize under irradiation, even 2-alkoxy-6-vinylpyridines **2** have a chance to react slowly to make intramolecular dimers or pyridinophanes. Thus, qualitatively the Caldwell's prediction is also proved here in the reactions of some vinylpyridines.

Synthesis of [2.*n*](2,6)Pyridinocrownophanes 3 and Their Conformation. Precursor olefins **2** were prepared from the reaction of dibromides **1**.

The photocycloaddition of **2** was carried out under the irradiation using a 400-W high-pressure mercury lamp through a Pyrex filter. The irradiation to precursor olefin (**2c**) in toluene afforded desired product (**3c**) in 51% yield. Since the low yield (40% yield) was recorded in MeCN, toluene was used as solvent for other photoreactions.

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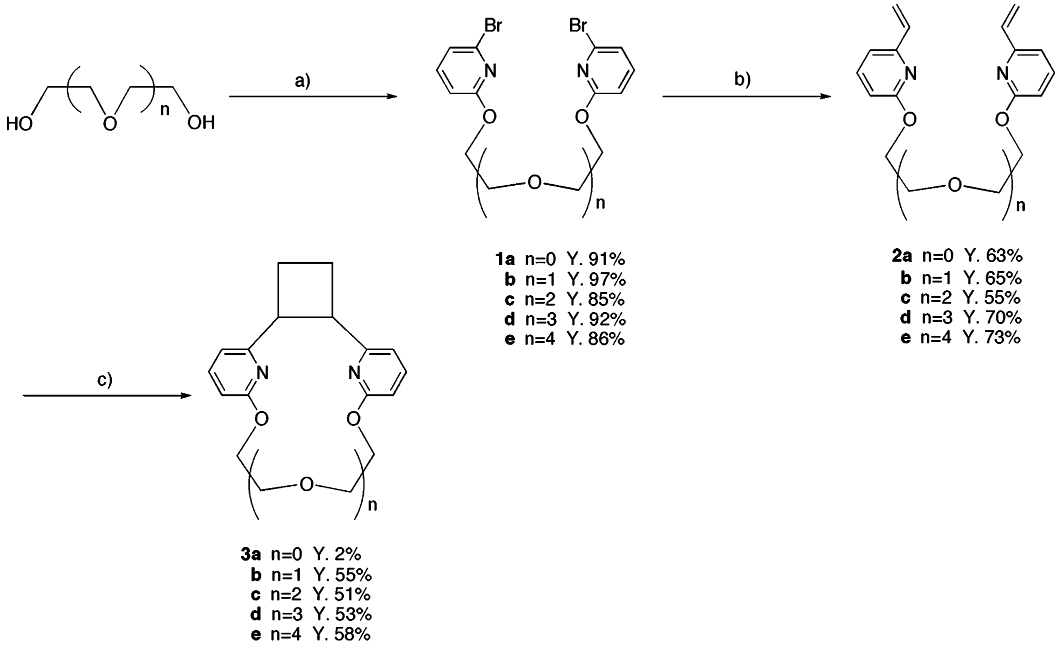
SCHEME 1[a]

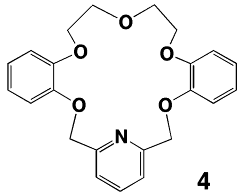


[a] Conditions: (a) (1) NaH/THF, (2) 2,6-dibromopyridine/THF−DMF; (b) $CH_2{=}CHSn(n\text{-}Bu)_3$, $Pd(PPh_3)_4$, 2,6-di-*tert*-butyl-4-methyphenol/toluene; (c) *hν* (>280 nm)/toluene.

TABLE 2. Extraction of Heavy Metal Cations with Ligands

	extractability[a] (%)							
ligand	Ag^+	Pb^{2+}	Cu^{2+}	Mn^{2+}	Zn^{2+}	Ni^{2+}	Co^{2+}	Fe^{3+}
3a	15 (4.9)	0 (4.8)	0 (4.3)	0 (6.5)	0 (6.1)	0 (6.3)	0 (7.2)	6 (1.5)
3b	33 (4.9)	0 (4.8)	0 (4.3)	0 (6.5)	0 (6.1)	0 (6.3)	0 (7.2)	6 (1.5)
3c	48 (5.2)	0 (4.7)	0 (4.4)	0 (5.4)	0 (6.1)	0 (5.8)	0 (6.4)	0 (1.7)
3d	42 (5.3)	0 (4.7)	0 (4.5)	0 (5.2)	0 (6.0)	0 (5.8)	0 (6.4)	0 (1.7)
3e	23 (5.2)	0 (4.7)	0 (4.4)	0 (5.3)	0 (5.9)	0 (5.7)	0 (6.4)	0 (1.6)
4	59 (5.5)	10 (5.6)	0 (4.1)	0 (6.3)	2 (6.2)	0 (6.7)	0 (6.9)	0 (1.6)

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



4

From ^{1}H NMR analysis **3** was found to have *cis*-cyclobutane ring which was proved by the specific methine proton signals at δ 3.98−4.08 (in $CDCl_3$).[20] All compounds showed three sets of aromatic proton peaks, which were high-field shifted, compared to those of **2** (Δδ = 0.25−0.39).

Pyridinophanes **3** have at least syn- and anti-conformers. According to VT-NMR experiments, however, the conformers were not assigned one other, because even at 183 K they did not give well splitted signals but broad ones, so that syn- and anti-conformers cannot be assigned.

Complexing Behavior toward Heavy Metal Nitrates. Pyridinocrownophanes **3** were used as extractants for heavy metal nitrates in the liquid−liquid system in order to obtain one of the preliminary information regarding their complexing ability. To attain their highest extractability for each heavy metal cation by **3** the pH value of an aqueous solution was adjusted as high as possible not to precipitate the hydroxides as mentioned in the Experimental Section. The results are summarized in Table 2 together with that of dibenzopyridino-18-crown-6 **4** as a reference compound. Compound **4** efficiently extracted Ag^+ but not much Pb^{2+}.

Pyridinocrownophane **3a** slightly extracted both Ag^+ and Fe^{3+}. The low efficiency for Ag^+ ion is because its cavity size, ca. 1.3 Å of diameter estimated from the space-filling model, is too small to accommodate Ag^+ ion (2.32 Å of diameter).[21] Therefore, this affinity is most likely due to the formation of a perching complex, which is generally less stable than a nesting complex.[22] The 1:1

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[20] Nishimura, J.; Ohbayashi, A.; Doi, H.; Nishimura, K.; Oku, A. *Chem. Ber.* **1988**, *121*, 2019.

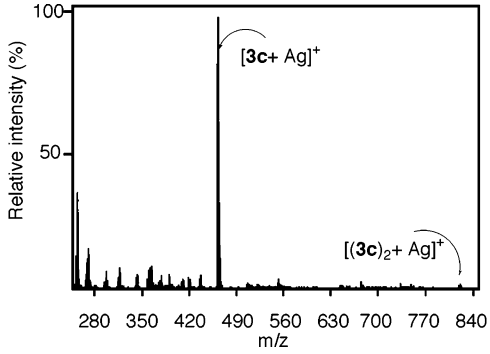

FIGURE 2. ESI-MS of **3c** in MeCN–H_2O containing equimolar amounts of $AgNO_3$.

complexation between **3a** and Ag^+ ion was proved by ESI-MS analysis as mentioned below. On the other hand, compounds **3b**–**e** moderately extracted Ag^+ ion with high selectivity, except for **3b** having some extractability to Fe^{3+} ion. Hence, it is clarified that host **3** works generally as an Ag^+-ionophore, but for the efficient complexation toward Ag^+ ion it requires to possess larger number of ethereal oxygen atoms than three in the linkage. Although the cavity size of compound **3e** seemed too large to fit Ag^+ ion, they still showed high affinity toward the cation. In this case, the host compound formed the special kind of complex with changing its conformation into the three-dimensional tennis-ball-seam fashion which was observed for the complexation between valinomycin and K^+ ion.[23]

Electrospray ionization mass spectroscopy (ESI-MS) is one of the most simple and useful methods to disclose the complexing behavior of host compounds with cations in a polar homogeneous system.[24,25] Gokel and Wang clarified that the K^+/Na^+ binding selectivity of 18-crown-6 studied by ESI-MS in methanol is in good agreement with that obtained by ion-selective electrode techniques in the same solvent.[26] We have been examined alkali metal cation selectivity of four-bridged crownophanes[27] and bisbenzocrown ethers bridged by cyclobutane ring[28] by ESI-MS. The interaction between **3** and silver nitrate was also examined by the same technique reported previously.[29]

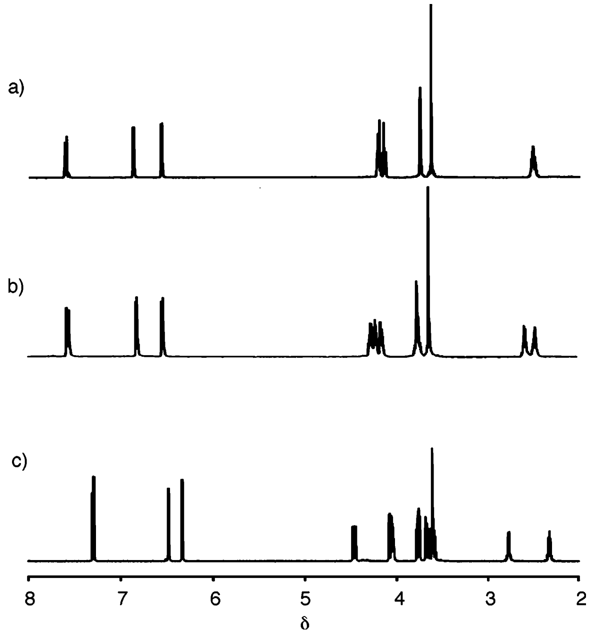

FIGURE 3. ^1H NMR spectra of **3c** in the absence and presence of $AgClO_4$. $[\mathbf{3c}] = 2.0 \times 10^{-2}$ M. $[Ag^+]/[\mathbf{3c}]$: (a) 2, (b) 1, and (c) 0.

TABLE 3. Stability Constant (K_a) of 3 and Reference 4[a]

ligand	3a	3b	3c	3d	3e	4
K_a	65	102	557	27	22	231

[a] Determined in MeCN-d_3 at 25 °C.

The major 1:1 complex and negligible 2:1 (host/guest) complexes between **3a**–**e** and Ag^+ ion were observed (see Figure 2 for example). Note that any free host molecule is not observed in the spectra despite the equilimolar amounts of **3** and silver nitrate used. Therefore, this result indicates an efficient interaction between **3** and the cation, though the complexing abilities of phanes **3a**–**e** to the cation cannot be directly compared one other by this analysis. The 1:1 stoichiometry of the complexation between the phanes and the cation observed provides an important information in order to determine their association constant by the curve fitting method based on ^1H NMR titration.

As shown in Figure 3, the sharp changes of the ^1H NMR chemical shifts and the peak shapes were observed at the addition of equimolar $AgClO_4$ to **3**. Even when more than 2 mol of the salt was added, no change was observed. It is suggested that the conformation of **3** is finally fixed to a certain form, where pyridine moieties and polyether moieties cooperatively acted as ligating sites for the cation.

Determination of Association Constants (K_a). To evaluate thoroughly the complexing ability in the homogeneous system, we measured the association constant (K_a) of **3** and **4** with Ag^+ ion by ^1H NMR titration in MeCN-d_3 at 25 °C (Table 3). Their values were in the range of 22–557 M^{-1}, and the order of K_a of **3** agrees with that of Ag^+ extractability listed in Table 2. Namely, **3c** shows the highest extractability marks the highest K_a in the series. The K_a constant of **4** with Ag^+ ion was determined to be 231 M^{-1}. Although K_a for **3c**–Ag^+ ion ($K_a = 557$ M^{-1}) is larger than that of the **4**–Ag^+ ion, the extractability of **3c** is lower than that of **4**. The result is most likely due to the difference in their lipophilicity, which strongly governs the transfer process of complexes

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(29) Inokuma, S.; Kimura, K.; Funaki, T.; Nishimura, J. *Heterocycles* **2001**, *55*, 447.

from the aqueous phase into the organic phase. The lipophilicity of **4** having two benzene rings is actually larger than that of **3c**.

In conclusion, the [2 + 2] photocycloaddition was extended to the preparation of pyridinocrownophanes **3**. In the extraction experiment, **3** showed high affinity toward Ag^+. Although their extractability was lower than that of the conventional ionophore **4**, their Ag^+ selectivity was higher than that of **4**.

The extension of [2 + 2] photocycloaddition to the preparation of **3** will bring a bonanza not only in photochemical field, but also in the design of new receptors and ionophores.

Experimental Section

Apparatus. ^1H NMR spectra were recorded on an FT NMR spectrometer (500 MHz) using tetramethysilane as an internal standard. Coupling constants (J) are reported in hertz. Elemental analysis was carried out in the Technical Research Center for Instrumental Analysis, Gunma University. Electrospray ionization mass spectra (ESI-MS) were obtained 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.

Reagents. THF and toluene were 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 **4** 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 $Fe(NO_3)_3$ were used after drying in vacuo. Aqueous solution was prepared with distilled, deionized water.

Preparation of α,ω-Bis(3′-bromo-2′-pyridyl)oligo(oxyethylene) 1. Oligo(oxyethylene) (0.0267 mol) was added to a suspension of NaH (60% in oil, 2.53 g, 0.066 mol, washed with *n*-hexane by decantation) in THF (20 mL). After the evolution of hydrogen gas had ceased, a DMF (30 mL) solution of 2,6-dibromopyridine (0.106 mol) was added to the suspension with stirring for 0.5 h at room temperature. Then the mixture was stirred for 4 h at 65 °C. After cooling to room temperature, to this reaction mixture was added a 1:1 ethanol solution of chloric acid to neutralize excess NaH. The organic solution was filtered and evaporated in vacuo. The residue was purified by recrystallization or column chromatography (SiO_2, a gradient mixture of toluene and ethyl acetate) to afford **1**. **1a**: yield 91%; white solid; mp 113−114 °C (a mixed solvent of toluene and ethyl acetate); ^1H NMR ($CDCl_3$) δ 7.43 (2H, dd, J = 8.2, 7.4), 7.08 (2H, d, J = 7.4), 6.74 (2H, d, J = 8.2), 4.65 (4H, s). Anal. Calcd for $C_{12}H_{10}Br_2N_2O_2$: C, 38.53; H, 2.69; N, 7.49. Found: C, 38.58; H, 2.72; N, 7.37. **1b**: yield 97%; white solid; mp 84−85 °C (a mixed solvent of toluene and ethyl acetate); ^1H NMR ($CDCl_3$) δ 7.40 (2H, dd, J = 8.9, 8.2), 7.05 (2H, d, J = 8.2), 6.72 (2H, d, J = 8.9), 4.49 (4H, t, J = 9.5), 3.89 (4H, t, J = 9.5). Anal. Calcd for $C_{14}H_{14}Br_2N_2O_3$: C, 40.22; H, 3.38; N, 6.70. Found: C, 40.28; H, 3.40; N, 6.63. **1c**: yield 85%; white solid; mp 86−87 °C (a mixed solvent of toluene and ethyl acetate); ^1H NMR ($CDCl_3$) δ 7.40 (2H, dd, J = 8.2, 7.3), 7.04 (2H, d, J = 7.3), 6.72 (2H, d, J = 8.2), 4.47 (4H, t, J = 9.5), 3.84 (4H, t, J = 9.5), 3.72 (4H, s). Anal. Calcd for $C_{16}H_{18}Br_2N_2O_4$: C, 41.58; H, 3.93; N, 6.06, Found: C, 41.75; H, 3.99; N, 6.03. **1d**: yield 92%; pale yellow viscous liquid; ^1H NMR ($CDCl_3$) δ 7.40 (2H, dd, J = 8.3 & 8.2), 7.04 (2H, d, J = 8.2), 6.72 (2H, d, J = 8.3), 4.47 (4H, t, J = 9.5), 3.84 (4H, t, J = 9.5), 3.71−3.66 (8H, m). Anal. Calcd for $C_{18}H_{22}Br_2N_2O_5$: C, 42.71; H, 4.38; N, 5.53. Found: C, 42.48; H, 4.36; N, 5.66. **1e**: yield 86%; white solid; mp 36−37 °C; ^1H NMR ($CDCl_3$) δ 7.42 (2H, dd, J = 8.3, 7.3), 7.03 (2H, d, J = 7.3), 6.72 (2H, d, J = 8.3), 4.46 (4H, t, J = 9.4), 3.83 (4H, t, J = 9.4), 3.70−3.65 (12H, m). Anal. Calcd for $C_{20}H_{26}Br_2N_2O_6$: C, 43.66; H, 4.76; N, 5.09. Found: C, 43.70; H, 4.78; N, 5.12.

Preparation of α,ω-Bis(6-vinylpyridyl)oligo(oxyethylene) 2. A solution of **1** (10.9 mmol), tri-*n*-butylvinylstannane (8.28 g, 26.1 mmol), $Pd(PPh_3)_4$ (0.84 g, 7.24 × 10^{-4} mol), and 2,6-di-*tert*-butyl-4-methylphenol (10 mg) in toluene (100 mL) was heated to reflux for 20 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 **2**. **2a**: yield 63%; white solid; mp 66−67 °C; ^1H NMR ($CDCl_3$) δ 7.54 (2H, dd, J = 8.3, 7.3), 6.85 (2H, d, J = 7.3), 6.72 (2H, dd, J = 17.2, 10.5), 6.64 (2H, d, J = 8.3), 6.26 (2H, dd, J = 17.2, 1.8), 5.41 (2H, dd, J = 10.5, 1.8), 4.75 (4H, s). Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.56; H, 6.14; N, 10.41. **2b**: yield 65%; white solid; mp 28−29 °C; ^1H NMR ($CDCl_3$) δ 7.47 (2H, dd, J = 8.2, 7.3), 6.78 (2H, d, J = 7.3), 6.67 (2H, dd, J = 17.2, 10.5), 6.64 (2H, d, J = 8.2), 6.24 (2H, dd, J = 17.2, 1.8), 5.37 (2H, dd, J = 10.5, 1.8), 4.49 (4H, t, J = 10.1), 3.91 (4H, t, J = 10.1). Anal. Calcd for $C_{18}H_{20}N_2O_3$: C, 69.21; H, 6.45; N, 8.97, Found: C, 68.91; H, 6.50; N, 8.87. **2c**: yield 55%; white solid; mp 31−32 °C; ^1H NMR ($CDCl_3$) δ 7.50 (2H, dd, J = 8.2, 7.3), 6.81 (2H, d, J = 7.3), 6.68 (2H, dd, J = 17.2, 10.5), 6.65 (2H, d, J = 8.2), 6.24 (2H, dd, J = 17.2, 1.7), 5.39 (2H, dd, J = 10.5, 1.7), 4.53 (4H, t, J = 9.7), 3.87 (4H, t, J = 9.7), 3.74 (4H, s); HRMS (EI) calcd for $C_{20}H_{24}N_2O_4$ (M^+) 356.1736, found 356.1764. **2d**: yield 70%; pale yellow viscous liquid; ^1H NMR ($CDCl_3$) δ 7.50 (2H, dd, J = 8.2, 7.3), 6.81 (2H, d, J = 7.3), 6.68 (2H, dd, J = 17.3, 10.5), 6.66 (2H, d, J = 8.2), 6.25 (2H, dd, J = 17.3, 1.5), 5.38 (2H, dd, J = 10.5, 1.5), 4.53 (4H, t, J = 9.8), 3.87 (4H, t, J = 9.8), 3.73−3.68 (8H, m); HRMS (EI) calcd for $C_{22}H_{28}N_2O_5$ (M^+) 400.1998, found 400.1994. **2e**: yield 73%; viscous liquid; ^1H NMR ($CDCl_3$) δ 7.51 (2H, dd, J = 8.2, 7.3), 6.81 (2H, d, J = 7.3), 6.68 (2H, dd, J = 17.2, 10.5), 6.66 (2H, d, J = 8.2), 6.24 (2H, dd, J = 17.2, 1.6), 5.39 (2H, dd, J = 10.5, 1.6), 4.53(4H, t, J = 9.8), 3.86 (4H, t, J = 9.7), 3.72−3.66 (8H, m); HRMS (EI) calcd for $C_{24}H_{32}N_2O_6$ (M^+) 444.2260, found 444.2263.

Preparation of Pyridinocrownophane 3. The photocycloaddition was carried out by a conventional method developed.[17] Into a 300-mL flask with a magnetic stirring bar and N_2 inlet was placed 2.00 × 10^{-4} mol of olefin **2** dissolved in toluene (200 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, ethanol) to afford **3**. **3a**: yield 8%; viscous liquid; ^1H NMR ($CDCl_3$) δ 7.17 (2H, dd, J = 8.3, 7.1), 6.39 (2H, d, J = 7.1), 6.33 (2H, d, J = 8.3), 5.47−5.38 (2H, m), 4.52−4.43 (2H, m), 4.03−3.98 (2H, m), 2.88−2.84 (2H, m), 2.41−2.36 (2H, m); HRMS (EI) calcd for $C_{16}H_{16}N_2O_2$ (M^+) 268.1211, found 268.1223. **3b**: yield 58%; pale yellow solid; mp 59−60 °C; ^1H NMR ($CDCl_3$) δ 7.20 (2H, dd, J = 7.9, 7.3), 6.41 (2H, d, J = 7.3), 6.29 (2H, d, J = 7.9), 5.04−4.99 (2H, m), 4.21−4.14 (4H, m), 4.08−4.05 (2H, m), 3.81−3.76 (2H, m), 2.94−2.90 (2H, m), 2.38−2.33 (2H, m). Anal. Calcd for $C_{18}H_{20}N_2O_3$: C, 69.21; H, 6.45; N, 8.97, Found: C, 69.24; H, 6.59; N, 8.93. **3c**: yield 51%; pale yellow viscous liquid; ^1H NMR ($CDCl_3$) δ 7.25 (2H, dd, J = 7.9, 7.4), 6.41 (2H, d, J = 7.4), 6.39 (2H, d, J = 7.9), 4.53−4.48 (2H, m), 4.18−4.14 (2H, m), 4.04−4.02 (2H, m), 3.86−3.82 (2H, m), 3.76−3.66 (6H, m), 2.80−2.76 (2H, m), 2.40−2.34 (2H, m); HRMS (EI) calcd for $C_{20}H_{24}N_2O_4$ (M^+) 356.1736, found 356.1737. **3d**: yield 53%; pale yellow solid; mp 91−92 °C; ^1H NMR ($CDCl_3$) δ 7.28 (2H, dd, J = 8.0, 7.3), 6.46 (2H, d, J = 7.3), 6.43 (2H, d, J = 8.0), 4.32−4.27 (2H, m), 4.21−4.17 (2H, m), 4.02−3.99 (2H, m), 3.78−3.74 (2H, m), 3.71−3.63

(10H, m), 2.75−2.70 (2H, m), 2.39−2.35 (2H, m); HRMS (EI) calcd for $C_{22}H_{28}N_2O_5$ (M^+) 400.1998, found 400.1996. **3e**: yield 51%; pale yellow viscous liquid; ^{1}H NMR ($CDCl_3$) δ 7.26 (2H, dd, $J = 8.2, 7.3$), 6.45 (2H, d, $J = 7.3$), 6.41 (2H, d, $J = 8.2$), 4.27−4.20 (4H, m), 4.01−3.98 (2H, m), 3.81−3.59 (16H, m), 2.76−2.70 (2H, m), 2.39−2.31 (2H, m); HRMS (EI) calcd for $C_{24}H_{32}N_2O_6$ (M^+) 444.2260, found 444.2260.

Calculation of $\gamma(r_c)$. Semiempirical calculations were made using the PM3 Hamiltonian included in the MOPAC pakage (WinMOPAC ver. 2.0). The ground-state geometries of vinylpyridines were optimized by the PM3 method. Then the energies, E_S and E_T, for the Franck−Condon excited singlet (S_1) and triplet (T_1) state were calculated by taking into account configuration interaction (CI = 4).

Solvent Extraction of Heavy Metal Nitrates. A CH_2Cl_2 solution of pyridinocrownophane (1.0×10^{-4} M, 5.0 mL) and an aqueous metal nitrate solution (1.0×10^{-1} M, 5.0 mL), whose pH value was adjusted as high as possible unless the hydroxides were precipitated, were shaken in a 20 mL test tube with a ground-glass stopper at ambient temperature (ca. 20 °C) for 1 h. Two liquid phases were separated, and the equilibrium pH of the aqueous phase was measured. An aliquot (2 mL) of the organic phase was evaporated under reduced pressure, and then dilute HNO_3 aqueous solution (2 mL) was added to the residue, and finally the extracted cation was analyzed by atomic absorption analysis.

ESI-MS Measurement of 3 in the Presence of Silver Nitrate. The sample solution ($MeCN-H_2O$ [4:1 (v/v)]) contained **3** (1.0×10^{-4} M) and silver nitrate (1.0×10^{-4} M).

^{1}H NMR Titration of 3 with Silver Perchlorate. A MeCN-d_3 solution of **3** (2.0×10^{-2} M) was prepared, its 500 μL portions were placed in an NMR tube, and the solvent level was marked. A second solution was made in MeCN-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 to the mark by evaporation. The spectrum was then recorded again. This procedure was repeated until the salt concentration is reached 10 equiv of that of **3**. The chemical shifts of the aromatic proton of **3** before and after each addition of the salt solution were plotted. From the titration curves obtained the association constants (K_a) were determined by nonlinear least-squares fitting method for 1:1 complexation, which was proved by the ESI-MS analysis (Figure 2).

Supporting Information Available: $\gamma(r_c)$ values of vinylpyridine derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

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