

Supporting Information for:

**Modulation of Metal Recognition by a Novel Calix[4]arene
Bearing Two Bipyridine Units as a Molecular Gate**

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Experimental Section

General Methods. All chemicals were reagent grade, and used without further purification. All solvents used in the reactions were purified before use. THF was purified by distillation from benzophenone ketyl under argon atmosphere before use.

Column chromatography was performed with Merck silica gel 60 (70-230 mesh). Melting points were determined on a Yanaco melting point apparatus, and not corrected. ^1H NMR spectra were recorded on a Bruker AC300 spectrometer at 300 MHz. ^{13}C NMR spectrum was recorded on a Bruker AC300 spectrometer at 75 MHz. In both NMR measurements, tetramethylsilane was used as an internal standard. ESI-MS spectrum was recorded on a Perkin-Elmer Sciex API-100 spectrometer. Elemental analysis was performed at Chemical Analysis Center, University of Tsukuba.

Synthesis of 1. A mixture of **2** (253 mg, 0.25 mmol), 60% NaH (37 mg, 0.93 mmol), and dry THF (15 ml) was refluxed for 40 min. To the mixture was added methyl bromoacetate (0.9 ml, 9.5 mmol), and the mixture was refluxed for 23 h. The resultant precipitates were removed by filtration, and washed with CH₂Cl₂. The organic filtrates were combined and the solvent was removed under reduced pressure. The residue was mixed with CHCl₃, washed with water, and dried over anhydrous MgSO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (SiO₂, toluene:EtOAc = 2:3) to give compound **1** (138 mg, 47%) as pale brown solid. **1**: mp 205.0-207.0 °C. ¹H NMR (300 MHz, CDCl₃) δ 1.01 (s, 18H), 1.11 (s, 18H), 2.40 (s, 6H), 3.05 (d, *J* = 13 Hz, 4H), 3.67 (s, 6H), 4.38 (d, *J* = 13 Hz, 4H), 4.45 (s, 4H), 5.25 (s, 4H), 6.69 (s, 4H), 6.80 (s, 4H), 7.62 (dd, *J* = 8, 2 Hz, 2H), 7.86 (dd, *J* = 8, 2 Hz, 2H), 8.29-8.32 (m, 4H), 8.51 (d, *J* = 2 Hz, 2H), 8.79 (d, *J* = 2 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 18.3, 31.3, 31.4, 31.7, 33.7, 33.9, 51.5, 70.9, 73.8, 119.9, 120.7, 125.2, 125.3, 133.0, 133.2, 133.4, 134.0, 137.4, 138.2, 145.1, 145.2, 149.5, 150.5, 152.4, 152.6, 153.6, 155.5, 170.5. ESI MS observed *m/z* 1157.7 ([M+H]⁺). Anal. Calcd. for **1**•0.5H₂O: C, 76.19; H, 7.34; N, 4.80. Found: C, 76.03; H, 7.09; N, 4.80.

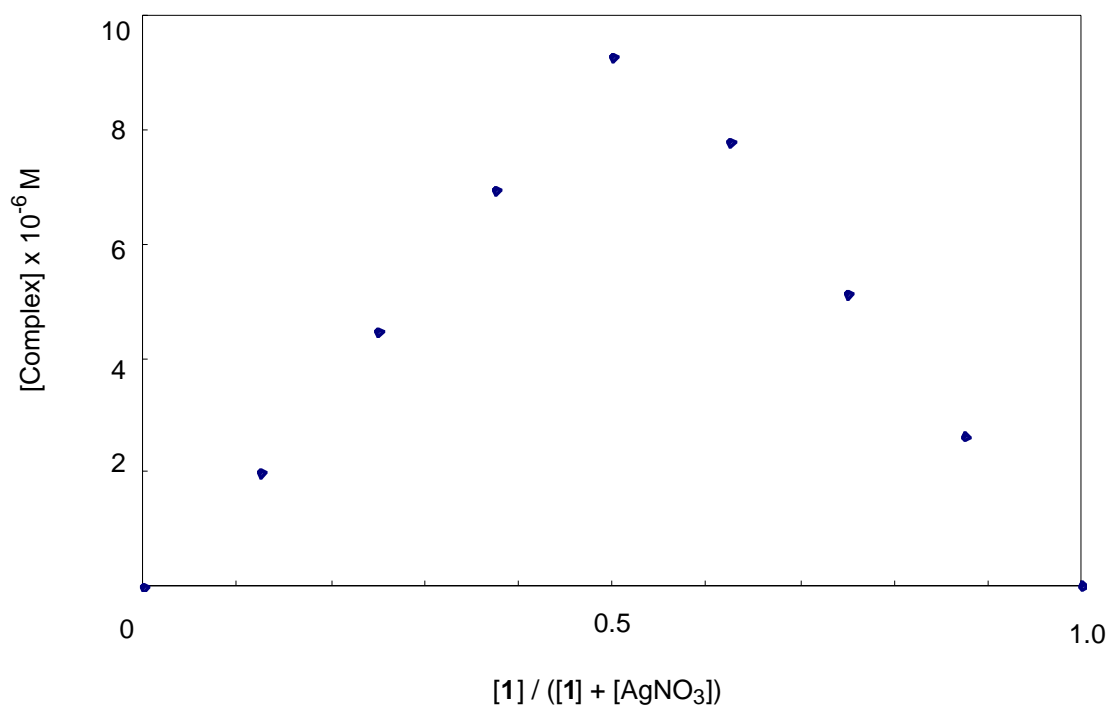


Figure 5. Job Plot for Complexation between **1** and AgNO_3 Using the Absorption at 290 nm. $\text{CH}_2\text{ClCH}_2\text{Cl} : \text{CH}_3\text{CN} = 10 : 1$, $[\mathbf{1}] + [\text{AgNO}_3] = 2.0 \times 10^{-5} \text{ M}$.

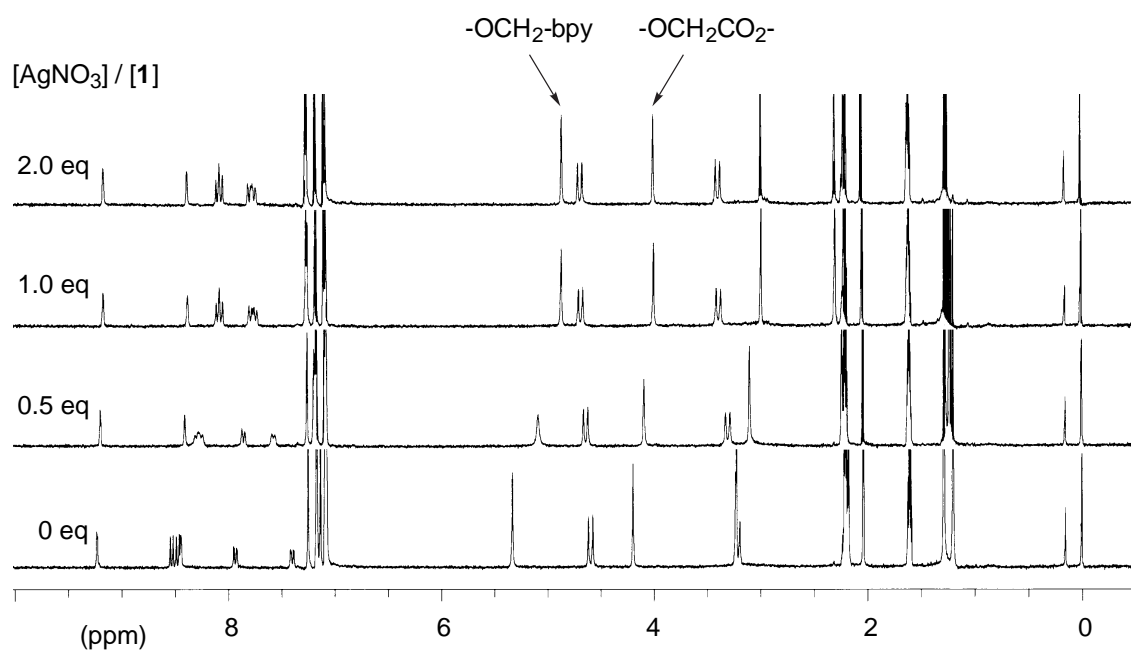


Figure 6. ^1H NMR Spectral Changes of **1** by the Addition of AgNO_3 at 300 MHz in toluene- d_8 : $\text{CD}_3\text{CN} = 6 : 5$. $[\mathbf{1}] = 2.00 \times 10^{-3}$ M.

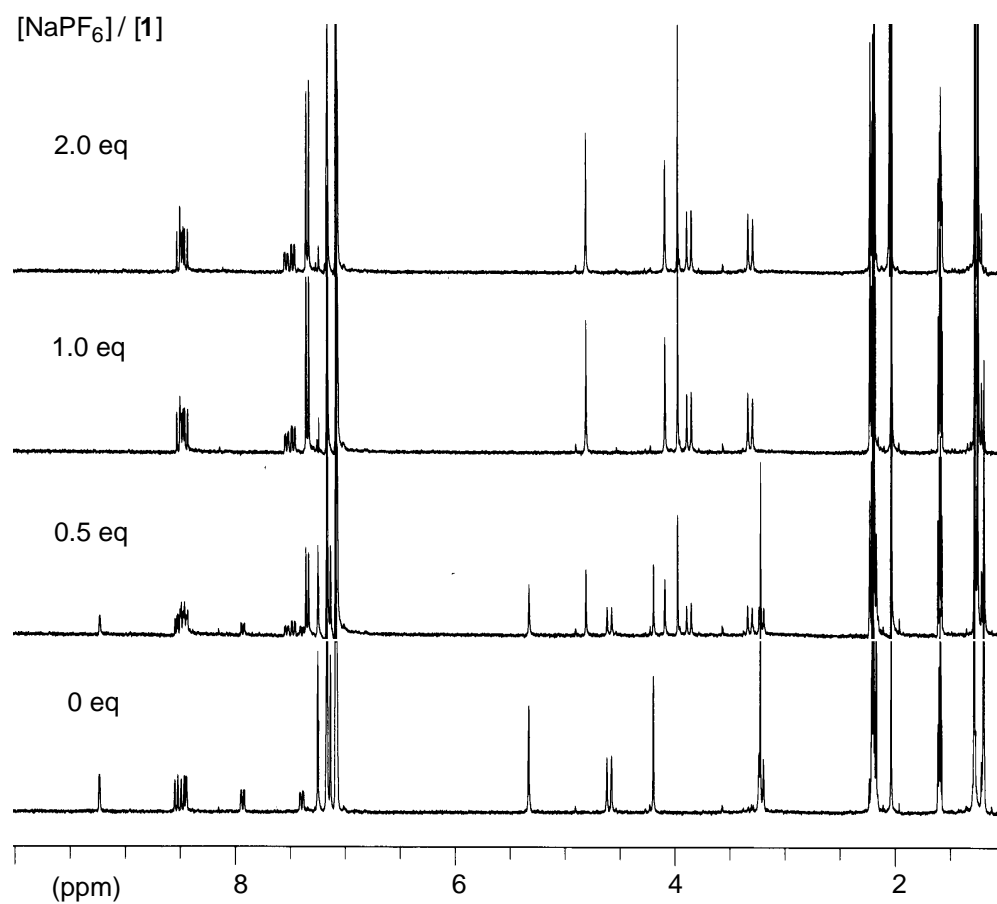


Figure 7. ^1H NMR Spectral Changes of **1** by the Addition of NaPF_6 at 300 MHz in toluene- d_8 : $\text{CD}_3\text{CN} = 6 : 5$. $[\mathbf{1}] = 2.00 \times 10^{-3} \text{ M}$.

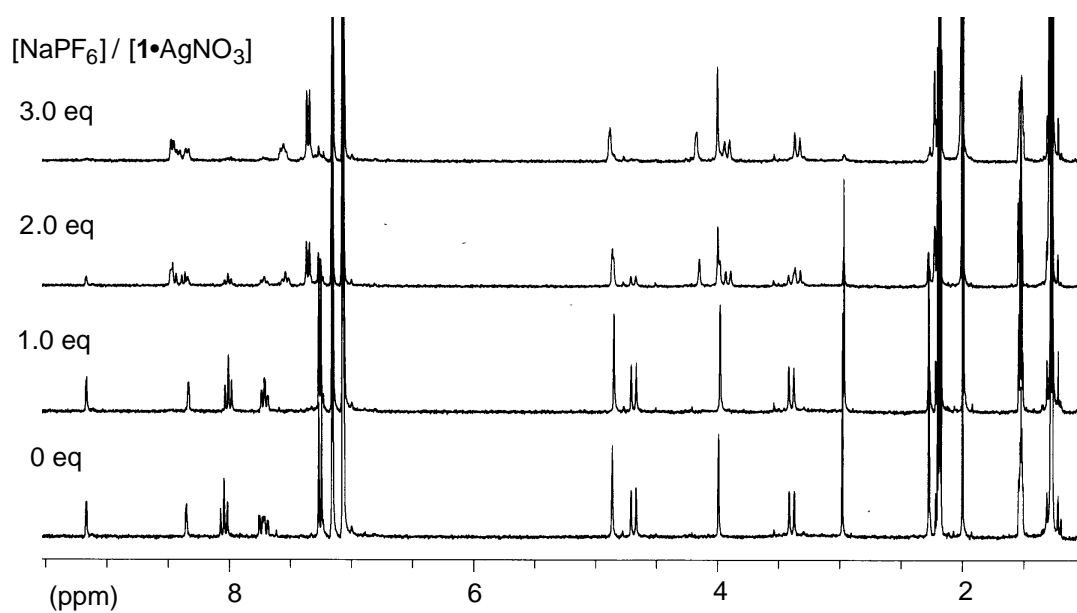


Figure 8. ^1H NMR Spectral Changes of $1\bullet\text{AgNO}_3$ by the Addition of NaPF_6 at 300 MHz in $\text{toluene-}d_8 : \text{CD}_3\text{CN} = 6 : 5$. $[1\bullet\text{AgNO}_3] = 2.00 \times 10^{-3} \text{ M}$.