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Binding Properties of *p*-(Phenylazo)calixarenes for Metal Ions

Eisaku Nomura,* Hisaji Taniguchi, and Yoshio Otsuji†
Industrial Technology Center of Wakayama Prefecture, Ogura, Wakayama 649-62
† Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 593

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The binding properties of *p*-(phenylazo)calix[*n*]arenes (n=6 and n=4) for metal ions have been studied. The calixarenes show a highly selective binding ability toward Ag^+, Hg^+, and Hg^{2+}. This property can be explained in terms of a metal ion-induced azo/hydrazone tautomerism. The Ag^+ ion forms complexes with the azocalixarenes by binding with their hydrazone tautomers.

Calixarenes are macrocyclic oligomers that can be obtained by a base-catalyzed condensation of *p*-substituted phenols with formaldehyde. Their properties are of considerable interest and now finding wide chemical applications.1) For example, these compounds can be utilized as inclusion compounds,2) selective complexing agents for metal ions,3) and catalysts.4) Recently, Shinkai's group and also our group reported physical and chemical properties of azocalixarene derivatives.5—10) In the course of our studies, we found that *p*-(phenylazo)calix[6]arene (**1a**) has a strong binding ability toward heavy metal ions such as Ag^+, Hg^+, and Hg^{2+} ions.5) We have extended this study in order to clarify the characteristic nature of binding properties of *p*-(phenylazo)calix[*n*]arenes **1a** (n=6) and **1b** (n=4) for metal ions.

Results and Discussion

Tautomeric Properties. It is known that 4-phenylazo-1-naphthol undergoes an azo/hydrazone tautomerism in polar media and the quinone-hydrazone form is favored in highly polar solvents.11) Shinkai and co-workers reported that a water-soluble *p*-(4-trimethylammoniophenylazo)calix[4]arene exists in the structure containing two pairs of quinhydrone-like component in acidic aqueous solutions (see Scheme 1), and the pK_a values of four phenolic OH groups in aqueous solution are 0.5, 2.0, 10.0, and ca. 13, respectively.10)

The electronic spectrum of azocalix[6]arene **1a** in an aqueous dioxane changed markedly upon adding an aqueous NaOH solution (Fig. 1a). A similar spectral change was also observed for azocalix[4]arene **1b** (Fig. 1b). A more clear-cut spectral change was observed for a monomer model **3** (Fig. 1c). In the case of **3**, the absorption at 460 nm that arises from the hydrazone form increased and the absorption at 356 nm that arises from the azo form decreased with increasing the added amount of NaOH solution. An isosbestic point appeared at 388 nm. However, no isosbestic point was observed for **1a** and **1b**. Noteworthy was that the spectral changes for **1a** and **1b** were small in a low concentration range ($<1\times10^{-2}$ mol dm^{-3}) of added NaOH.

It is known that in calix[4]arenes, cone conformation is favored by strong intramolecular hydrogen-bonding interactions among four phenolic OH groups.1) For **1a** and **1b**, however, it would be reasonable to suppose that the molecules are stabilized by two or three pairs of intramolecular hydrogen-bonding interactions between undissociated phenolic OH groups and neighboring dissociated phenolate anions in the low concentration range of added NaOH (see Scheme 1). This assumption accounts for the experimental results that much larger quantities of NaOH are needed for the azo/hydrazone tautomeric shift of **1a** and **1b**, compared to that of **3**. The results of Figs. 1a and 1b also indicate that the intramolecular hydrogen-bonding ability of **1b** is stronger than that of **1a**.

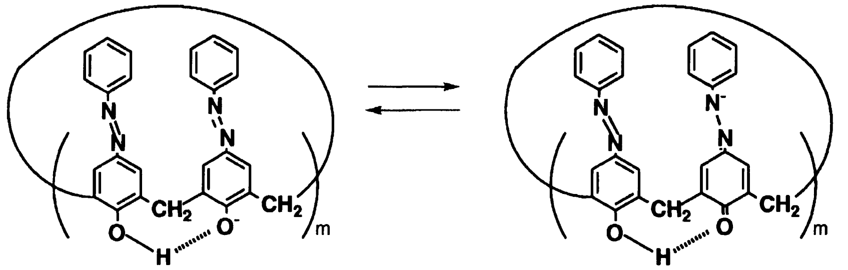
Binding Properties for Metal Ions. The binding ability of **1a** and **1b** toward metal ions was evaluated by means of solvent extraction of their metal picrates from aqueous phase into $CHCl_3$, and it was compared with that of related compounds. The results are summarized in Table 1. The azocalixarenes showed the binding ability toward Ag^+, Hg^+, and Hg^{2+}, but not toward Na^+, K^+, Zn^{2+}, and Pb^{2+}. Furthermore, the binding ability of **1a** was much greater than that of **1b** (Chart 1). The monomer model **3** exhibited a significant binding ability toward all the metal ions, but showed no selectivity (Chart 2). *O*-Methylated azocalixarenes **2a** and **2b**, and also *p*-*t*-butylcalix[6]arene exhibited no binding ability toward all the metal ions.

Figure 2 shows the electronic spectra of **1a** in aqueous THF solutions in the presence of several metal nitrates. Unfortunately, the electronic spectra of **1a** in the presence of Na^+, K^+, Hg^+, and Hg^{2+} ions were

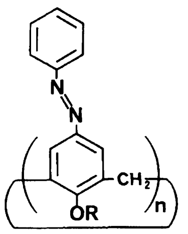
Table 1. Solvent Extraction of Metal Picrates with Azocalixarenesa)

Calixarene	Metal picrates extracted/%						
	Na^+	K^+	Ag^+	Hg^+	Hg^{2+}	Zn^{2+}	Pb^{2+}
1a	0	0	$22_{\pm1}$	$8_{\pm1}$	$18_{\pm2}$	0	0
1b	0	0	Trace	$4_{\pm2}$	$5_{\pm1}$	0	0
2a	0	0	0	0	0	0	0
2b	0	0	0	0	0	0	0
3	$31_{\pm1}$	$7_{\pm2}$	$23_{\pm4}$	$31_{\pm2}$	$32_{\pm1}$	$24_{\pm1}$	$28_{\pm1}$

a) Aqueous phase: [metal nitrate]=1.0×10^{-2} mol dm^{-3}, [picric acid]= 1.8×10^{-5} mol dm^{-3}; organic phase: $CHCl_3$, [calixarene]=1.0×10^{-3} mol dm^{-3} for **1a**, **1b**, **2a**, and **2b**, 6.0×10^{-3} mol dm^{-3} for **3**: temp: 25 °C; time: 24 h.



Scheme 1.



	n	R
1a:	6	H
b:	4	H
2a:	6	CH_3
b:	4	CH_3

Chart 1.

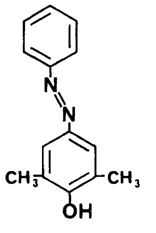


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Chart 2.

not obtained because of low solubility of the metal nitrates in aqueous THF solution. Upon adding Ag^+, the absorbance at λ_{max} 360 nm decreased markedly with a slight bathochromic shift, and a new absorption appeared at around 450 nm. A similar spectral change was observed for **1b**. For **2a** and **2b**, such a spectral change was not observed. For **3**, the absorbance at λ_{max} 356 nm increased, but without any change in the spectral shape.

The spectral changes for **1a** and **1b** can be explained in terms of their azo/hydrazone tautomeric equilibria. This explanation is based on the similarity in the spectral patterns of Figures 1a, 1b, and 1c and those of Fig. 2. In $CHCl_3$ and THF, **1a** and **1b** exist mainly in the azo form, but they are converted partially into the hydrazone form upon complexation with metal ions, particularly with Ag^+ ion. A plausible structure of the Ag complex is shown in formula **4** in which the azo group and the hydrazono nitrogen are coordinated to Ag^+ ion (Chart 3).

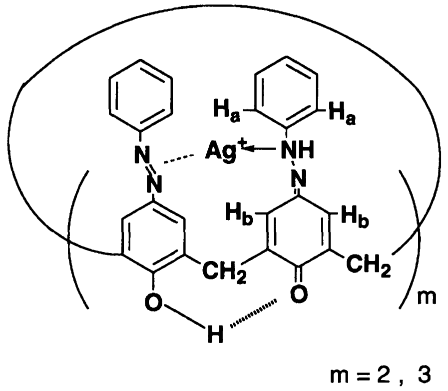

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Chart 3.

The stoichiometry of this complexation reaction was estimated from the spectral change of **1a** in the presence of $AgNO_3$. Although the accurate stoichiometry could not be determined from simple spectral measurements, plots of the absorbance at λ_{max} in the spectra of **1a** in THF against the molar ratio $[AgNO_3]/[\mathbf{1a}]$ suggested that **1a** forms a complex with two or more than two equivalents of $AgNO_3$. Similar experiments suggested that **1b** forms a complex with one or more than one equivalent of $AgNO_3$, and **3** forms a complex with $AgNO_3$ approximately in a 1 : 1 molar ratio. We then estimated stability constants of these silver complexes. In a low concentration region of $AgNO_3$, it can possibly be assumed that all the compounds form 1 : 1 complexes with $AgNO_3$ and their stability constants may be expressed by the following equation:

$$\mathrm{L} + \mathrm{AgNO_3} \overset{K_c}{\rightleftharpoons} \mathrm{L(AgNO_3)}$$

where L is ligand **1a**, **1b** or **3**. The K_c values for 1 : 1 complexes of the ligands with $AgNO_3$ in THF at 25 °C were evaluated from spectral measurements by virtue of the Benesi–Hildebrand equation[12] (see Experimental). The evaluated K_c values for **1a**, **1b**, and **3** were 2.2×10^4, 7.1×10^4, and 3.6×10^4 $dm^3\,mol^{-1}$, respectively. These values indicate that **1a**, **1b**, and **3** have relatively strong binding ability toward Ag^+ ion.

The complexation of **1a** with Ag^+ ion was evidenced by ^1H NMR spectroscopy. Table 2 shows the ^1H NMR

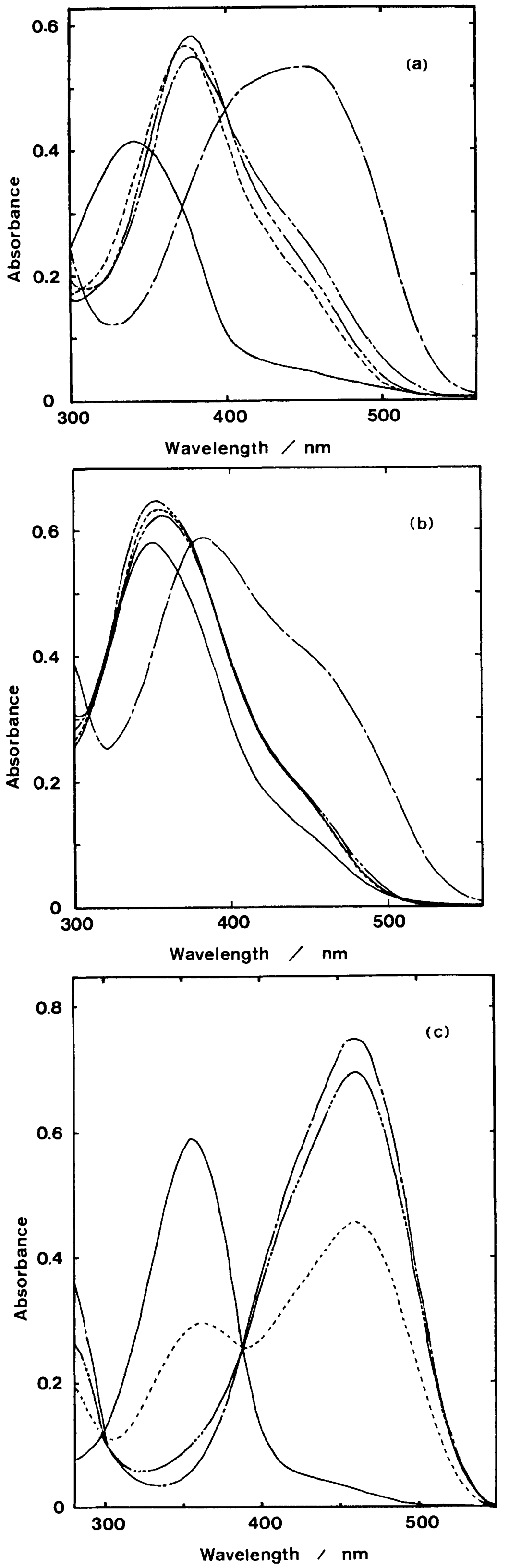

Fig. 1. Absorption spectra of **1a** (a) (5.0×10^{-6} mol dm^{-3}), **1b** (b) (1.0×10^{-5} mol dm^{-3}), and **3** (c) (2.5×10^{-5} mol dm^{-3}) in dioxane–water (1 : 1, w/w) in the presence of NaOH (none, —; 1.0×10^{-4} mol dm^{-3}, - - -;1.0×10^{-3} mol dm^{-3}, – - - –; 1.0×10^{-2} mol dm^{-3}, – - –; 1.0×10^{-1} mol dm^{-3}, - - -).

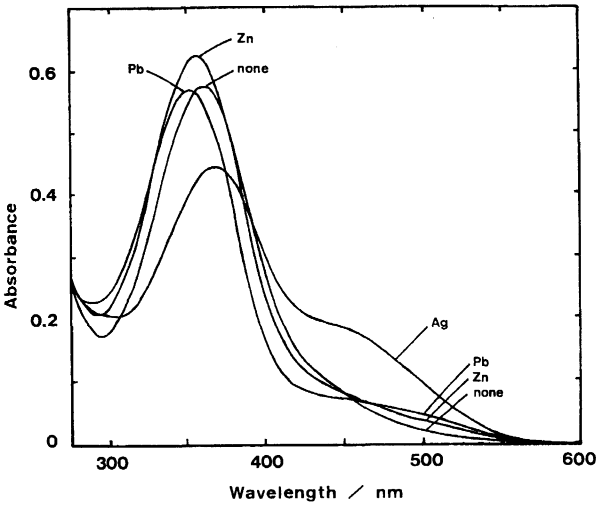

Fig. 2. Absorption spectra of **1a** (5.0×10^{-6} mol dm^{-3}) in THF–water (99 : 1, v/v) in the presence of metal nitrates (1.0×10^{-3} mol dm^{-3}).

Table 2. ^{1}H NMR Data for **1a** in THF-d_8 in the Absence or Presence of CF_3SO_3Ag[a)]

	1a/ppm	
		In the presence of Ag^+
Ar–H	7.37—7.52 (m) 7.76—7.85 (m)	6.59 (bs) 7.23—7.55 (m) 7.77—7.88 (m) 8.57 (bs)
Ar_2–CH_2	4.12 (s)	3.77—4.67 (m)

a) Spectra were measured at ambient temperature.

spectral data for **1a** in THF-d_8 in the presence and absence of CF_3SO_3Ag. The ^{1}H NMR spectrum of **1a** changed greatly upon addition of CF_3SO_3Ag. A new signal appeared at $\delta=6.59$ can be assigned to the H_b protons in **4**. It is worth noting in this connection that the corresponding proton signal in calix[4]quinone is observed at $\delta=6.70$ in DMSO-d_6.[7)] The other new signal appeared at $\delta=8.57$ can be assigned to the H_a protons in **4**. Unfortunately, the ^{1}H NMR spectrum of the silver complex of **1b** could not be obtained because of its very low solubility in any organic solvents.

The 1 : 3 complex of **1a** was able to isolate as a solid material. Standing of a mixture of **1a** and large excess of CF_3SO_3Ag (**1a**: CF_3SO_3Ag=1 : 12) in THF at room temperature for 24 h gave precipitates. The elemental analysis showed that the precipitated complex contained **1a** and CF_3SO_3Ag in 1 : 2.6 ratio. In a similar manner, the silver complex of **1b** was obtained. This complex contained **1b** and CF_3SO_3Ag in 1 : 1 ratio. However, these complexes could not be purified by recrystallization because of their low solubility in organic solvents. It was also found that the composition of the complexes largely depends on their solubility. In fact in the case of **1b**, a 1 : 1 complex was precipitated out when CF_3SO_3Ag was added to a THF solution of **1b** because of its low solubility, and complexes having other compositions could not be obtained by this method.

An important feature of this complexation reaction is that **1a** and **1b** show a binding ability for metal ions that belong to soft acid in Pearson's classification[13] and these metal ions are captured on the hydrazono nitrogen rather than on the hydroxyl oxygen. This is consistent with the HSAB principle, since the hydrazono nitrogen is a much softer basic center than the hydroxyl oxygen.[13]

In the case of **3**, the stabilization by intramolecular hydrogen bonding, such as that shown in **4**, is impossible. Hence, metal ions are captured unselectively by **3** on the hydroxyl oxygen. This was supported by the fact that no UV spectral change occurred when metal ions were added into the THF solution of **3**.

Experimental

Electronic spectra were recorded on a Hitachi 556 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX90A (90 MHz) spectrometer. IR spectra were recorded on a Hitachi EPI-G3 spectrometer. Elemental analyses were carried out with a Yanagimoto CHN corder MT-3 instrument. Melting points were measured with a Yanagimoto micro melting point apparatus and uncorrected. Thermal analyses were performed with a Seiko SSC 5200 instrument.

***p*-(Phenylazo)calix[6]arene (1a).** A freshly prepared aqueous HCl solution of benzenediazonium chloride (10.8 mmol) was added dropwise to a stirred mixture of $CH_3CO_2Na\cdot3H_2O$ (2.0 g, 7.3 mmol) and calix[6]arene[14] (1.0 g, 1.57 mmol) in tetrahydrofuran (THF)–water (5:2, 14 cm^3) under ice-cooling over a period of 15—20 min. After stirring further for 3 h, water (50 cm^3) was added and the resulting mixture was stirred for 15—30 min. The precipitates were separated by filtration, washed with water, dried and recrystallized from DMSO. The orange solid (0.9 g 45%) was dried in vacuo at 100 °C for 4 d to give **1a** as a dark red solid; mp 279 °C (decomp): IR (KBr) 3400, 1600, 1475, 1123, 772, and 695 cm^{-1}; ^{1}H NMR (pyridine-d_5) δ=4.37 (12H, s, ArCH$_2$Ar), 7.3—8.2 (42H, m, ArH), and 11.97 (6H, s, OH); ^{13}C NMR (pyridine-d_5) δ=34.4, 122.8, 124.7, 129.3, 129.8, 130.0, 145.5, 153.8, and 161.2. Found: C, 74.43; H, 4.77; N, 13.06%. Calcd for $C_{78}H_{60}N_{12}O_6$: C, 74.27; H, 4.79; N, 13.33%.

***p*-(Phenylazo)calix[4]arene (1b).** This compound was prepared by modifying the method reported by Shinkai et al.[10] A freshly prepared aqueous HCl solution of benzenediazonium chloride was added dropwise to a stirred mixture of calix[4]arene (1.0 g, 2.36 mmol) and $CH_3CO_2Na\cdot3H_2O$ (2.0 g, 14.7 mmol) in THF–water–pyridine (5:1:1, 30 cm^3) under ice-cooling over a period of 10—15 min. After stirring further for 5 h, the reaction mixture was poured onto water (200 cm^3) and allowed to stand for several hours. The resulting black solid was separated by filtration, washed with water, and dried. Recrystallization of the solid twice from CHCl$_3$–MeOH (2:1) gave **1b** as orange crystals (1.1 g, 50%); mp 325 °C (decomp) (lit,[10] mp>280°C (decomp)); IR (KBr) 3190, 1595, 1472, 1275, 1115, 768, and 688 cm^{-1}; ^{1}H NMR (CDCl$_3$, at 20 °C) δ=4.1 (8H, d, ArCH$_2$Ar), 7.4—7.9 (28H, m, ArH), and 10.27 (4H, s, OH); ^{13}C NMR (CDCl$_3$) δ=31.9, 122.6, 124.4, 128.3, 129.0, 130.5, 147.8, 151.3, and 152.7. Found: C, 74.28; H, 4.75; N, 13.13%. Calcd for $C_{52}H_{40}N_8O_4$: C, 74.27; H, 4.79; N, 13.33%.

***O*-Methyl-*p*-(phenylazo)calix[6]arene (2a).** A THF solution of methyl iodide (3.34 g, 23.5 mmol) was added at once to a mixture of **1a** (1.0 g, 0.793 mmol), KOH (1.3 g, 24 mmol), and benzyltrimethylammonium chloride (0.5 g) in THF–water (5:1, 12 cm^3). The mixture was stirred at 40 °C for 6 h, and poured onto water (200 cm^3). The resulting precipitates were separated by filtration, washed with water, dried, and then chromatographed on silica gel with CHCl$_3$–hexane (9:1). Recrystallization of the crude solid from CHCl$_3$–EtOH (2:1) gave **2a** as orange needles (0.4 g, 37%); mp 358 °C (decomp); IR (KBr) 1582, 1470, 1425, 1278, 1222, 1111, 1005, 768, and 688 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=3.37 (18H, s, OCH$_3$), 4.10 (12H, s, ArCH$_2$Ar), and 7.4—7.9 (42H, m, ArH); ^{13}C NMR (CDCl$_3$) δ=30.7, 60.6, 122.7, 124.0, 129.0, 130.6, 135.3, 148.5, 152.8, and 159.1. Found: C, 74.10; H, 5.39; N, 12.15%. Calcd for $C_{84}H_{72}N_{12}O_6\cdot C_2H_6O$: C, 74.22; H, 5.65; N, 12.08%.

***O*-Methyl-*p*-(phenylazo)calix[4]arene (2b).** This compound was prepared by a similar method to that described for **2a**. The crude product was purified by chromatography on silica gel with benzene and then by recyrstallization from benzene–MeOH (2:1). The purified product (0.3 g, 28%) was obtained as orange needles; mp 275—277 °C; IR (KBr) 1585, 1473, 1282, 1226, 1112, 1016, 770, and 690 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=3.1—4.6 (20H, m, OCH$_3$, ArCH$_2$Ar), and 7.1—8.1 (28H, m, ArH). Found: C, 75.01; H, 5.44; N, 12.30%. Calcd for $C_{56}H_{48}N_8O_4$: C, 74.98; H, 5.39; N, 12.49%.

2,6-Dimethyl-4-phenylazophenol (3). This compound was prepared from 2,6-dimethylphenol and benzenediazonium chloride by the method described in the literature,[15] and recrystallized from MeOH–water. The purified product was obtained as orange prisms; mp 94—95 °C (lit,[15] 95—96 °C).

Solvent Extraction. A chloroform solution (5 cm^3) of an azocalixarene (1.0×10^{-3} mol dm^{-3}) and an aqueous solution (5 cm^3) containing a metal nitrate (1.0×10^{-2} mol dm^{-3}) and picric acid (1.8×10^{-5} mol dm^{-3}) were combined and shaken for 24 h at 25 °C. The control experiment was carried out by making extraction using pure chloroform as extraction solvent without added azocalixarene. The extractability of the azocalixarene toward a metal ion was determined from the difference in absorbance due to the metal picrate in two aqueous phases which were obtained by the above two methods.

Stability Constants of Silver Complexes. The stability constant of a 1:1 complex of **1a**, **1b**, and **3** with AgNO$_3$ was determined from the following Benesi–Hildebrand type equation:[12]

$$\frac{1}{\varepsilon^{\mathrm{a}}-\varepsilon^{\mathrm{L}}}=\frac{1}{K_{\mathrm{c}}}\cdot\frac{1}{\varepsilon^{\mathrm{LM}}-\varepsilon^{\mathrm{L}}}\cdot\frac{1}{[\mathrm{AgNO_3}]}+\frac{1}{\varepsilon^{\mathrm{LM}}-\varepsilon^{\mathrm{L}}}$$

where ε^{L} is the molar absorption coefficient for the ligand, ε^{a} is the apparent molar absorption coefficient for the Ag complex, and $\varepsilon^{\mathrm{LM}}$ is the molar absorption coefficient for the pure Ag complex. The ε^{L} and ε^{a} values were determined from absorbances at $\lambda_{\max}$. The stability constant K_{c} value was evaluated graphically by plotting $1/(\varepsilon^{\mathrm{a}}-\varepsilon^{\mathrm{L}})$

against 1/[$AgNO_3$]. In this study, the concentration of the ligand was kept constant (5×10^{-6} mol dm^{-3} for **1a**, 1.0×10^{-5} mol dm^{-3} for **1b**, and 2.5×10^{-4} mol dm^{-3} for **3**), and the concentration of $AgNO_3$ was varied in the range: [$AgNO_3$]/[ligand]=0.5—2.0. All the spectra were measured in THF at 25 °C. The above plots gave a straight line and the K_c value was obtained from the slope and intercept of this line.

CF_3SO_3Ag Complex of 1a. To a solution of **1a** (25 mg, 1.98×10^{-5} mol) in THF (1 cm^3) was added CF_3SO_3Ag (62.4 mg, 2.42×10^{-4} mol). The mixture was allowed to stand for 24 h. The precipitates were separated by filtration and washed with THF (20 cm^3) to give a red powder; mp 288 °C (decomp); IR (KBr) 1590, 1468, 1273, 1030, 759, 680, and 640 cm^{-1}. Found: C, 50.04; H, 3.23; N, 8.68%. Calcd for $C_{78}H_{60}N_{12}O_6\cdot2.6CF_3SO_3Ag$: C, 50.17; H, 3.13; N, 8.71%.

CF_3SO_3Ag Complex of 1b. To a solution of **1b** (30 mg, 3.57×10^{-5} mol) in THF (2 cm^3) was added CF_3SO_3Ag (9.2 mg, 3.57×10^{-5} mol). The mixture was allowed to stand for three days. The precipitates were separated by filtration and washed with THF (20 cm^3) to give a brown powder; mp 263 °C (decomp); IR (KBr) 1595, 1465, 1275, 1025, 758, 681, and 630 cm^{-1}. Found: C, 57.72; H, 3.61; N, 10.10%. Calcd for $C_{52}H_{40}N_8O_4\cdot CF_3SO_3Ag$: C, 57.98; H, 3.67; N, 10.21%.

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