Synthesis of Macrocyclic Cage Compounds by Diamine−Dihalide One-Step Coupling Reaction

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Macropolycyclic cage compounds were synthesized by a direct reaction between diamines and bis(bromomethyl) compounds. The procedure for constructing the polycyclic cage structure is simple and straightforward. The macropolycyclic compounds obtainable from this cyclization procedure are three-dimensional cage compounds, and any other isomers were not obtained except for two examples. Benzene, pyridine, and aliphatic units could be introduced into the cage structure. The macrocycles that have strong cation affinity were obtained as their potassium complexes.

Introduction

Previously, we reported the synthesis and inclusion properties of polycyclic cage compounds, which have benzene (**1a**), fluorobenzene (**5b**), thiophene (**15**), pyridine (**2a**−**c**, **3a**, **4a**), and oxaethylene units (**13**).[1] The structures of parent compound **1a** and the coordination structures of the K^+ complexes of **3a**, **5b**, and **13** were proven by X-ray crystallographic analyses. The cage compounds containing more than four pyridine rings showed strong alkali cation affinity (Rb^+ selective), although they act as anion receptors in acidic media.[1c,d,g,i] The specific feature as cation receptor resulted from the convergence of pyridine lone pairs into the cavity. The resultant cation complexes are kinetically inert because the cavities are surrounded by aromatic ring walls. The cation inclusion ability strongly depends on the number of pyridine rings. The cages **2a**−**c** that have two pyridine rings showed poor cation affinities, in contrast to the formation of very stable complexes, $M^+ \subset$ **3** or **4**. By introducing some donor units into such a specific cage structure, we can observe even weak interaction toward cations because the interactions are amplified by the convergence of the functional groups. Furthermore, the solvent−guest species interactions are suppressed by the isolation of the guests from solvent molecules by the host molecules. Therefore, we are interested in the synthesis of a new series of cage compounds constructed using various donor units. These macropolycyclic compounds were synthesized by a direct coupling reaction between diamines and dihalides. Although several methods for preparing bicyclic or polycyclic compounds have been reported, almost all of them involve stepwise procedures that are sometimes tedious and require a lot of time.[2] In some cases, one-step cyclization methods are employed in the synthesis of cryptands, but these are limited to relatively small molecules.[3] By using the one-step coupling reaction described here, the cage compounds were obtained in a short time. In this paper, we describe the extension of this method to the synthesis of cage compounds that have various donor units.

Results and Disussion

Syntheses of Macropolycyclic Cage Compounds. The possible products (type **I**−**V**) from the direct coupling reaction between diamines and dihalides are shown in

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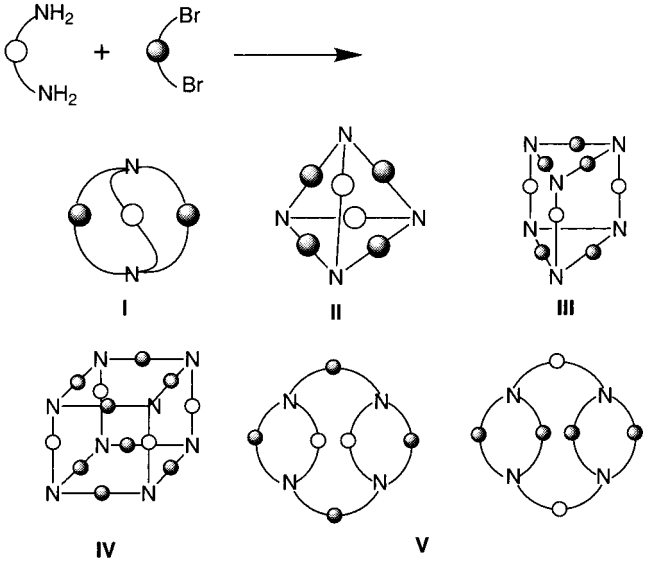
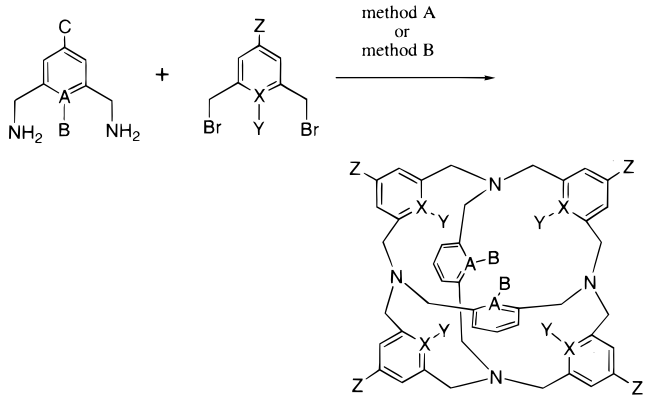
Scheme 1



Scheme 1. However, only tetrahedral cage compounds (type **II**) were obtained by the reaction between diamines and 1,3-(or 2,6-)bis(bromomethyl) compounds. Bond isomers of the type **II** compound (**V**), monomeric (**I**), trimeric (prismatic compound, **III**), and tetrameric (cubic compound, **IV**) compounds were not detected in all cases. Exceptionally, the reaction of 2,6-bis(bromomethyl)pyridine and 2,6-bis(aminomethyl)pyridine sometimes afforded a bond isomer (type **V**) along with cage compound **4a**. Previously, we reported the synthesis of a cubic compound (type **IV**) that was obtained by the reaction between 1,4-bis(aminomethyl)benzene and 1,4-bis(bromomethyl)benzene.[4] In this case, so-called "cubic cyclophane"[5] was obtained in 4.7% yield. The yield was significantly improved compared to the stepwise synthesis (0.24% from the starting 1,4-bis(bromomethyl)benzene). The cage compounds obtained from this procedure are listed in Figure 1. The main reaction products of this coupling reaction are the polymeric quaternary ammonium salts. Thus, the macropolycyclic products were easily isolated from the reaction mixture by a simple chromatographic technique and almost pure materials were obtained. The yields were low (~12.3%), but the method saves labor and time compared to stepwise synthesis. The homogeneous conditions (method A) and the phase-transfer conditions (PTC, method B) were employed in the coupling reaction (Scheme 2). By using 1,4-dioxane as a solvent in the homogeneous condition, the reaction is rapid because of the high reaction temperature. Almost all reaction products are insoluble polymeric compounds; therefore, the desired compounds are easily isolated. On the other hand, PTC is convenient because the starting amines are generated in situ from their HCl salts. The hydrochloride salt of the amine is easy to handle and store compared to the free base. For example, 2,6-bis(aminomethyl)pyridine is a low-melting and very hygroscopic compound, and the isolation of the free base is very tedious.[1b,6] The diamines used in this report were commercially available or were obtained by Gabriel synthesis, and in the latter case, the obtained amine hydrochlorides could be used without isolation of the free bases. In addition, as previously reported, the compounds **3a** and **4a**[1b] were obtained as their protonated form under homogeneous conditions and further deprotonation by alkaline treatment of the products was necessary. By employing PTC, the isolation of amines and deprotonation of the resultant macrocycles are simultaneously achieved in one-pot fashion. Thus, the phase-transfer condition, CH_2Cl_2−aqueous KOH/Bu_4NBr, is the best choice in these cases. Similar to **3a** and **4a**, compounds **3**, **4**, **7**, **8**, **12**, and **13** were obtained as their potassium complexes under PTC. In these cases, the counteranions of the obtained complexes were identical to those of the PT catalyst used in the reaction. Other compounds were obtained as the metal-free form. A template effect does not operate in this coupling reaction: the yields of cage compounds that are the metal-free form or K^+ complexes are not very different. The structure of $K^+ \subset$ **4a** is shown in Figure 2. The four bridgehead nitrogen atoms form a slightly distorted tetrahedron, and the potassium ion is placed at the center of the cavity. All nitrogen atoms coordinate to K^+ ion in octahedral fashion. The bond lengths, $K^+\cdots N$, are in the range of 307−326 pm, which is similar to that of $K^+ \subset$ **13**.[1i]

Scheme 2[a]



[a] Method A: 1,4-dioxane, reflux. Method B: *n*-Bu_4NBr, aqueous KOH/CH_2Cl_2, reflux.

The series of compounds have high melting (decomposition) points. Particularly, the decomposition point of **1c** is over 400 °C (417.2−418.8 °C), the highest among all of the amines ever known, to the best of our knowledge.

The structures of cage compounds **II** were determined by comparison of the NMR spectra with those of the bond isomers **V** and/or by the X-ray crystallographic analyses. The bond isomers (type **V**) were synthesized by the stepwise method via 2,11-diaza[3.3]metacyclophane and its derivatives or 2,11-diaza[3.3](2,6)pyridinophane.[7] In contrast to the cage type compound, **16d** (type **V** molecule) has a large planar cavity, and it showed inclusion phenomena toward organic guests.[8] In all cases, the NMR spectral patterns of type **V** compounds are completely

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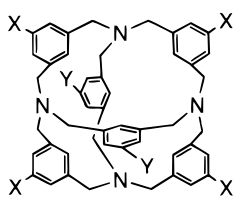
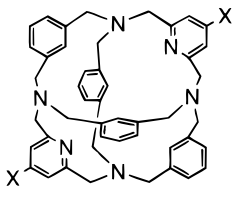


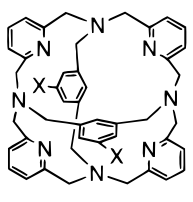
1

	X	Y	Yield
1a	H	H	(6.7 %)
1b	OMe	H	(3.2 %)
1c	t-Bu	H	(2.9 %)
1d	H	NO_2	(2.9 %)
1e	NO_2	H	(0.2 %)



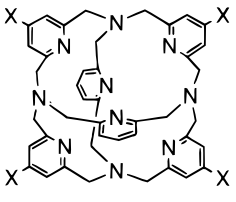
2

2a X = H (8.3 %)
2b X = OMe (12.3 %)
2c X =Cl (7.1 %)



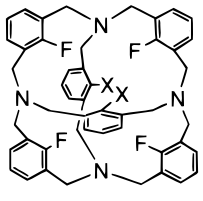
3*

3a X = H (4.3 %)
3b X = Br (2.3 %)



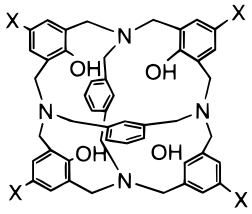
4*

4a X = H (2.4 %)
4b X = OMe (0.5 %)



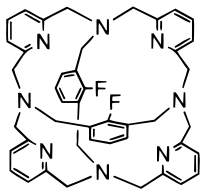
5

5a X = H (3.2 %)
5b X = F (2.3 %)

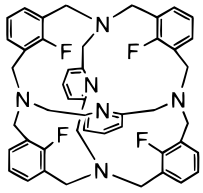


6

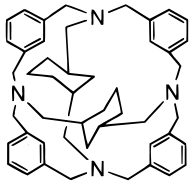
6a X = Cl (7.3 %)
6b X = Br (2.5 %)



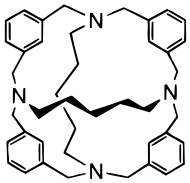
7* (1.1 %)



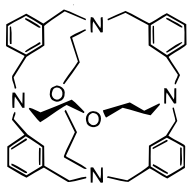
8* (0.8 %)



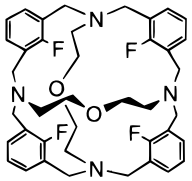
9 (2.4 %)



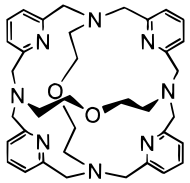
10 (4.1 %)



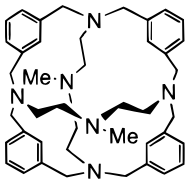
11 (3.9 %)



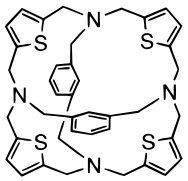
12* (1.3 %)



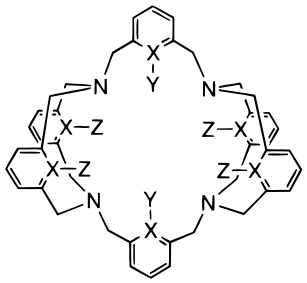
13* (1.0 %)



14 (1.2 %)



15 (4.1 %)



	X	Y	Z
16a	C	H	H
b	C	F	F
c	C	H	F
d	N		

Figure 1. Structures of cage compounds. *The yields were calculated as potassium complexes.

different from that of the cage compounds. For example, the spectrum of **1a** reflects the T_d symmetry of its structure, but that of **16a** consists of the signal of the metacyclophane moiety and that of the bridging *m*-xylylene moiety. The methylene proton signal of the metacyclophane moiety shows an A_2X_2 pattern. On the other hand, the methylene proton signal of the cage compounds that are constructed of the same units ap-

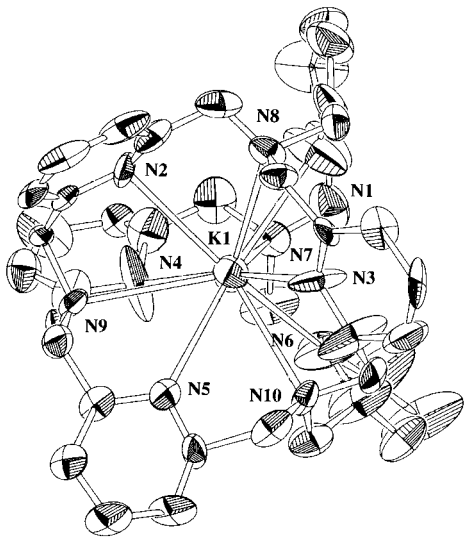


Figure 2. Molecular structure of compound $K^+ \subset$ **4a**. Thermal ellipsoids are drawn with 30% probability.

pears as a singlet. The methylene proton signal of the cage compounds that are constructed of two kinds of units shows A_2B_2 and a singlet as assumed by their molecular symmetry. These spectral features are common to the type **II** and **V** compounds. Among the bond isomers, the molecular structures of compounds **16a** and **16c**[1j] could be elucidated. The X-ray crystallographic analysis of **16a** showed that two conformers are included in the crystal (Figure 3). The [3.3]metacyclophane moieties of one of the two conformers are almost flat (α conformer), while in the other one these moieties are twisted and nearly perpendicular to each other (*β* conformer).

In this reaction, the electron-withdrawing group seems to decrease the coupling yield. The reaction of 4-chloro-2,6-bis(bromomethyl)pyridine and 1,3-bis(aminomethyl)-benzene did not yield any cyclic products despite several trials. The yield of **1e** employing 5-nitro-1,3-bis(bromomethyl)benzene was very low (0.2%). The hexanitro derivative **1f** was not obtained by the coupling method: it was prepared by direct nitration of **1a** (Scheme 3). The nitration of **1a** with mixed acid (64% HNO_3/98% H_2SO_4 = 2/3, v/v) at 65 °C for 2 h afforded a mixture of nitro compounds and starting material **1a**. The isolable products by silica gel chromatography were only the starting material (7%) and **1f** (13.5%). The remaining material was a complex mixture that could not be identified. To compare the product ratio, the nitration of *N*,*N*,*N*′,*N*′-tetramethyl-1,3-bis(aminomethyl)benzene was carried out. As a result, a product ratio of 4-nitro: 5-nitro = 2:5 was obtained, and the yields of 4- and 5-nitro compounds were 26 and 66%, respectively. The 2-nitro compound was generated in trace amounts. According to the ratio, the calculated yield of all 5-nitro derivative of **1a** was 13.2%, which is comparable to the experimental result. The color of the dinitro compound **1d** is yellow, while the tetranitro (**1e**) and hexanitro (**1f**) compounds are colorless. The UV−vis spectrum of the **1d** shows a weak band above 420 nm, which is the origin of the yellow color. This is ascribed to the weak CT interaction of the nitroxylylene and unsubstituted xylylene units.

As previously reported, the driving force of the strong cation affinity of the cage compounds **3a** and **4a** is the convergence of the lone pairs of the pyridine nitrogen into the cavity. In accord with this idea, introduction of functional groups into the cavity of the parent compound **1a** was attempted. Although the parent compound **1a** does not have cation affinity,[1] specific inclusion properties can be expected by the introduction of functional groups into the cavity. The fluorine atom is similar in size (147

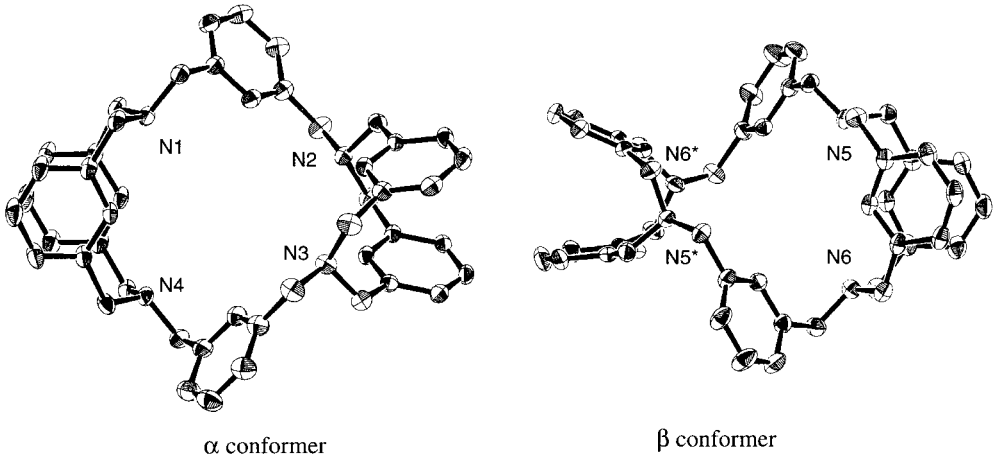
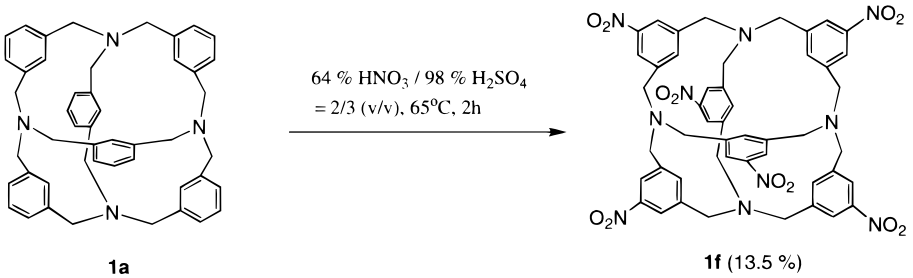
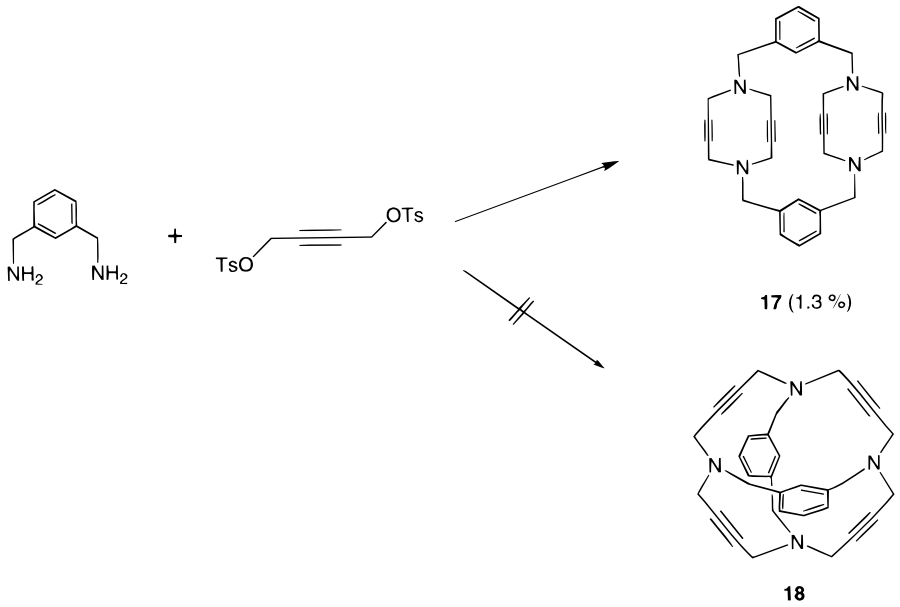


Figure 3. Molecular structure of compound **16a**. Thermal ellipsoids are drawn with 50% probability.

Scheme 3



Scheme 4



pm) to the hydrogen atom (120 pm);[9] therefore, tetrafluoro (**5a**) and hexafluoro (**5b**) compounds were obtained.[1h,j] Compounds **6a** and **6b,** which have four phenolic hydroxyl groups, were also obtained by the reaction of 1,3-bis(aminomethyl)benzene and 2,6-bis-(bromomethyl)-4-halophenol.[10] Because the fluorine atom and the hydroxyl group have an isoelectronic structure, the comparison of the cation affinity is interesting. However, the compound that has six phenolic hydroxyl groups has not been obtained so far. Similarly, the compounds that have four Cl or Br atoms were not obtained by the reactions of the corresponding diamines and dibromides.

The cage compounds **7** and **8** containing pyridine and fluorobenzene units were obtained as potassium complexes. It is noteworthy that compound **2a**, which consists of two pyridine rings and four benzene rings, is obtained in cation-free form, but compound **8** is isolated as its potassium complex; replacement of the two benzene units of **2a** by fluorobenzene units significantly increases the cation affinity. Recently, we elucidated that a fluorine atom connected to a benzene ring acts as a donor unit: hexafluoro compound **5b** forms stable cation complexes by C−F···M^+ interaction.[1h,j] In the case of compound **8**, it binds a K^+ ion by four C−F units and two pyridine nitrogen atoms. The studies of the cation complexation properties of **7** and **8** are currently in progress.

The synthesis of **18**, which contains acetylene units, was attempted in order to investigate the cation···π electron interaction. However, the reaction between 1,3-bis(aminomethyl)benzene and 1,4-butynediol ditosylate afforded bond isomer **17** instead of the desired cage compound **18** (Scheme 4). The compound **17** was reported by Gleiter et al., and all of the spectral and analytical data for the isolated product completely coincided with that of their report.[11] The compounds **10**−**14** containing flexible units such as cyclohexane or aliphatic chains were obtained by the one-step reaction. The compound **12** was obtained as its K^+ complex, although its benzene analogue **11** was obtained in metal-free form. Also here, the C−F units act as donor as in the case of compound **8**. In the case of the compounds that have aliphatic chains, it is difficult to distinguish between cage type **II** and type **V** by the NMR spectra. Therefore, the structure of compound **10** was determined by X-ray crystallographic analysis (Figure 4). The crystal structure of $K^+ \subset$ **13** was reported previously,[1i] and the structures of **12** and $K^+ \subset$ **12** will appear elsewhere.

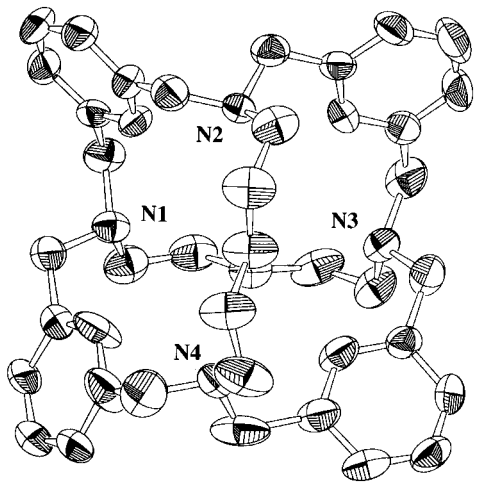
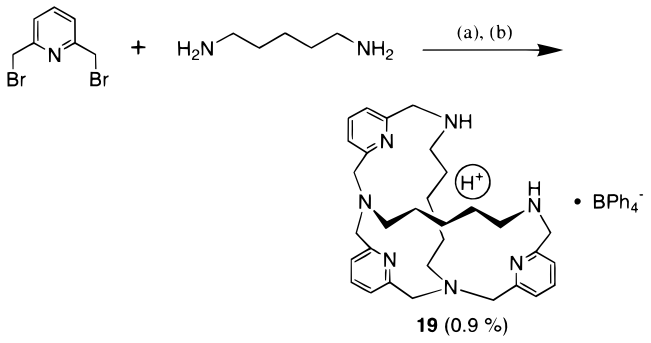


Figure 4. Molecular structure of compound **10**. Thermal ellipsoids are drawn with 50% probability.

Unexpectedly, the reaction between 2,6-bis(bromomethyl)pyridine and 1,5-diaminopentane under PTC afforded compound **19** consisting of three pyridine and two pentamethylene units in its monoprotonated form (Scheme 5). The monoprotonated salt was isolated in pure form from the reaction mixture by column chromatography followed by $NaBPh_4$ treatment. The characterization of the isolated compound was achieved by NMR, FAB-MS spectra, and elemental analysis. Despite using an

(9) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.
(10) de Mendoza, J.; Nieto, P. M.; Prados, P.; Sanchez, C. *Tetrahedron* **1990**, *46*, 671−682. The 2,6-bis(bromomethyl)-4-bromophenol was prepared by a method similar to that of 2,6-bis(bromomethyl)-4-chlorophenol.
(11) Gleiter, R.; Hövermann, K.; Ritter, J.; Nuber, B. *Angew. Chem.* **1995**, *107*, 867−869; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 789−791.

Scheme 5[a]



19 (0.9 %)

[a] Key: (a) CH_2Cl_2, aqueous KOH, Bu_4NBr; (b) $NaBPh_4$.

excess of the dibromide, the reaction gave hemi-cage compound **19**. It is interesting that it is obtained in monoprotonated form but not its potassium complex despite the strongly basic reaction conditions and the presence of a large excess of potassium ion. The treatment of **19** with aqueous KOH did not give the proton-free compound or its K^+ complex. An attempt to prepare compound **21** containing longer ethyleneglycol units than **13** was performed under PTC. The reaction between 2,6-bis(bromomethyl)pyridine and 1,2-bis(2-aminoethoxy)-ethane gave 2:1 cyclocondensation product **20** (type **I**) as its monoprotonated form instead of type **II** compound **21** (Scheme 6). A similar result was reported by Bradshaw et al. They performed the reaction of 1,3-bis(aminomethyl)benzene and 1,2-bis(2-iodoethoxy)ethane or diethyleneglycol-bis(2-iodoethyl)ether in CH_3CN.[3h] The corresponding cryptand (type **I**) was isolated as the major product, and 4:2 condensation products (type **II** and/or type **V**) were obtained as minor products. However, in our case, the obtained macropolycyclic product was **20** and other isomers were not detected.

Conclusion

The simple coupling reaction described here does not require special reagents and is useful for the synthesis of three-dimensional cage compounds. Because the reaction and workup are very simple, this method saves time and labor. By changing the construction units, potential cation receptors having different strengths of cation affinity could be obtained. The specific cation affinity and selectivity are expected by the combination of donor units. Especially, by introducing some functional groups in the cavity (pyridine lone pairs or C−F), interaction between a cation and functional groups was observed. The studies of inclusion phenomena of cations or anions by cage compounds containing functional groups (C−F, OH, pyridine, ether oxygen, and −NMe−) are currently in progress.

Experimental Section

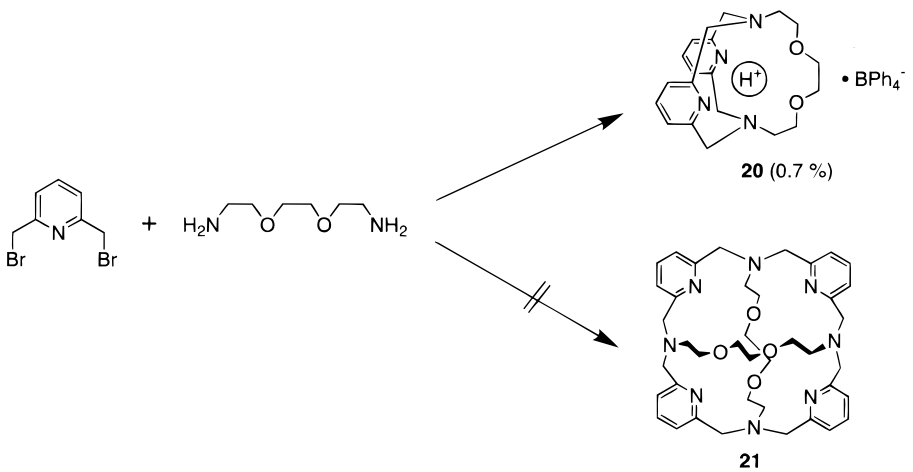
General Methods. All melting points were measured in Ar or N_2 sealed tubes and were uncorrected. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ with TMS as an internal standard. Mass spectra were recorded with *m*-NBA as a matrix. Two types of coupling reaction conditions were employed for the synthesis of macrocycles. The reaction under homogeneous conditions was carried out by using 1,4-dioxane as a solvent (method A). The reaction under phase-transfer conditions was carried out by using CH_2Cl_2−aqueous KOH as a solvent−base component, and *n*-Bu_4NBr was employed as a phase-transfer catalyst (method B). The yields were based on the starting dibromides. The quantities of the solvents included in the analytical samples were confirmed by the ^{1}H NMR spectra.

The ratio of the diamines and dihalides is not 1:2. Excess amounts of diamines are employed because they act as a base in method A. When the reaction was carried out in a ratio of diamine/dihalide = 1:2, we always recovered the halide after the workup. Thus, the halides were used in smaller amount than the theoretical amount both in method A and B.

Compound 1b (Method A). A solution of 3.00 g (22.0 mmol) of 1,3-bis(aminomethyl)benzene in 250 mL of 1,4-dioxane was vigorously stirred and heated under reflux. To this mixture was added a solution of 1,3-bis(bromomethyl)-5-methoxybenzene[12] (6.00 g, 20.4 mmol) in 150 mL of 1,4-dioxane over a period of 4 h. Additional stirring and refluxing were continued for 5 h. The reaction mixture was filtered, and the solvent was removed under reduced pressure. Column chromatography on alumina (C_6H_6) of the resultant oily product afforded a white powder, which was recrystallized from *n*-hexane−CH_2Cl_2 (white powder, 130 mg, 3.2%): mp > 285 °C dec; ^{1}H NMR δ 8.26 (bs, 2H), 7.91 (bs, 4H), 7.03 (t, J = 7 Hz, 2H), 6.93 (d, J = 7 Hz, 4H), 6.49 (s, 8H), 3.67 (s, 12H), 3.50 (bs, 24H); MS (FAB) *m*/*z* 800 (94, M^+). Anal. Calcd for $C_{52}H_{56}N_4O_4$: C, 77.97; H, 7.05; N, 6.99. Found: C, 78.17; H, 7.29; N, 6.83.

Compound 1c (Method A). This compound was prepared from the reaction between 1,3-bis(aminomethyl)benzene and 1,3-bis(bromomethyl)-5-*tert*-butylbenzene in 1,4-dioxane. Column chromatography of the resultant material on alumina (C_6H_6) followed by recrystallization from benzene afforded colorless prisms (2.9%): mp 417.2−418.8 °C dec; ^{1}H NMR δ 8.38 (s, 2H), 8.22 (s, 4H), 7.10−7.01 (m, 6H), 7.01 (s, 8H), 3.52

Scheme 6



20 (0.7 %)

21

(bs, 24H), 1.25 (s, 36H); MS (FAB) *m/z* 905 (28, $M^+ + 1$). Anal. Calcd for $C_{64}H_{80}N_4 \cdot C_6H_6$: C, 85.49; H, 8.81; N, 5.70. Found: C, 85.17; H, 8.81; N, 5.80.

Compound 1d (Method B). A solution of 1,3-bis(bromomethyl)benzene (4.52 g, 17.1 mmol) in 100 mL of CH_2Cl_2 was added dropwise into a boiling mixture of 1,3-bis(aminomethyl)-5-nitrobenzene dihydrochloride (3.53 g, 13.9 mmol), 50 mL of 2 N aqueous KOH, and 300 mL of CH_2Cl_2 over a period of 5 h. Refluxing and stirring were continued for another 2 h. The organic phase was separated and evaporated. The resultant material was column chromatographed on silica gel with C_6H_6 as an eluent. Recrystallization from benzene afforded yellow needles (2.9%): mp > 305 °C dec; ^{1}H NMR δ 8.63 (s, 2H), 8.24 (s, 4H), 7.94 (s, 4H), 7.18 (t, J = 7 Hz, 4H), 7.07 (d, J = 8 Hz, 8H), 3.53 (bs, 24H); MS (EI) *m/z* 770 (9, M^+). Anal. Calcd for $C_{48}H_{46}N_6O_4$: C, 74.78; H, 6.01; N, 10.90. Found: C, 74.45; H, 6.06; N, 10.60.

Compound 1e (Method A). This compound was prepared from the reaction between 1,3-bis(aminomethyl)benzene and 1,3-bis(bromomethyl)-5-nitrobenzene. Column chromatography of the resultant material on alumina (C_6H_6) followed by recrystallization from *n*-hexane−CH_2Cl_2 afforded colorless fine needles (0.2%): mp > 315 °C dec; ^{1}H NMR δ 8.52 (s, 4H), 8.13 (s, 2H), 7.98 (s, 8H), 7.20 (t, J = 6 Hz, 2H), 7.11 (d, J = 7 Hz, 4H), 3.57 (bs, 24H); MS (SI) *m/z* 860 (5, M^+). Anal. Calcd for $C_{48}H_{44}N_8O_8 \cdot {}^1/_3C_6H_{14}$: C, 67.50; H, 5.51; N, 12.59. Found: C, 67.24; H, 5.54; N, 12.32.

Compound 1f. Compound **1a** (53 mg, 7.8×10^{-2} mmol) was dissolved in a mixture of HNO_3 (64%)/H_2SO_4 (98%) = 2/3 (v/v, 2 mL) and heated at 65 °C for 2 h. After the usual workup, the resultant mixture was subjected to preparative TLC (Merk PF_{254}) with CH_2Cl_2 as an eluent. Recrystallization from *n*-hexane−CH_2Cl_2 afforded a colorless powder (13.5%): mp > 304 °C dec; ^{1}H NMR δ 8.47 (s, 2H), 8.42 (s, 4H), 8.02 (s, 12H), 3.68 (s, 24H); MS (SI) *m/z* 950 (0.3, M^+). Anal. Calcd for $C_{48}H_{42}N_{10}O_{12} \cdot {}^2/_3CH_2Cl_2$: C, 58.02; H, 4.34; N, 13.90. Found: C, 57.96; H, 4.36; N, 13.93.

$K^+ \subset$ 3b·Br^- (Method B). This compound was prepared from the reaction between 1,3-bis(aminomethyl)-5-bromobenzene and 2,6-bis(bromomethyl)pyridine. After usual workup, the resultant material was column chromatographed on alumina (CH_2Cl_2−MeOH, 98/2, v/v). Recrystallization from CH_2Cl_2−MeOH afforded colorless needles (2.3%): mp > 235 °C dec; ^{1}H NMR δ 7.68 (t, J = 8 Hz, 4H), 7.38 (s, 4H), 7.26 (d, J = 8 Hz, 8H), 6.85 (s, 2H), 3.60 (d, J = 13 Hz, 8H), 3.50 (d, J = 13 Hz, 8H), 3.37 (s, 8H); MS (FAB) *m/z* 879 (14, [M ($^{79}Br_2$) + K]$^+$), 881 (29, [M (^{79}Br + ^{81}Br) + K]$^+$), 883 (21, [M ($^{81}Br_2$) + K]$^+$). Anal. Calcd for $C_{44}H_{42}N_8Br_3K \cdot {}^5/_2H_2O$: C, 52.50; H, 4.71; N, 11.13. Found: C, 52.61; H, 4.52; N, 11.26.

$K^+ \subset$ 4b·Br^- (Method B). This compound was prepared from the reaction between 2,6-bis(aminomethyl)pyridine dihydrochloride and 2,6-bis(bromomethyl)-4-methoxypyridine. Column chromatography of the resultant material on alumina (CH_2Cl_2−MeOH, 98/2, v/v) followed by recrystallization from *n*-hexane−CH_2Cl_2 afforded colorless fine needles (0.5%): mp > 208.1 °C dec; ^{1}H NMR δ 7.57 (t, J = 8 Hz, 2H), 7.11 (d, J = 8 Hz, 4H), 6.65 (s, 8H), 3.84 (s,12H), 3.52 (bs, 24H); MS (FAB) *m/z* 846 (86%, [M + K]$^+$). Anal. Calcd for $C_{46}H_{50}N_{10}O_4KBr$: C, 59.67; H, 5.44; N, 15.13. Found: C, 59.88; H, 5.59; N, 15.13.

Compound 6a (Method A). This compound was prepared from the reaction between 1,3-bis(aminomethyl)benzene and 2,6-bis(bromomethyl)-4-chlorophenol.[10] Column chromatography of the resultant material on silica gel (*n*-hexane−C_6H_6, 2/1, v/v) followed by recrystallization from CH_2Cl_2−MeOH afforded a white powder (7.3%): mp > 337 °C dec; ^{1}H NMR δ 10.67 (s, 4H), 8.77 (s, 2H), 7.14 (t, J = 8 Hz, 2H), 7.03 (d, J = 8 Hz, 4H), 6.97 (s, 8H), 4.37 (d, J = 14 Hz, 4H), 4.28 (d, J = 13 Hz, 4H), 4.11 (d, J = 13 Hz, 4H), 3.11 (d, J = 14 Hz, 4H), 3.07 (d, J = 13 Hz, 4H), 2.63 (d, J = 13 Hz, 4H); MS (FAB) *m/z* 880 (18, M^+ ($^{35}Cl_4$)), 881 (23, M^+ ($^{35}Cl_4$) + 1), 882 (28, M^+ ($^{35}Cl_3$ + ^{37}Cl)), 883 (25, M^+ ($^{35}Cl_3$ + ^{37}Cl) + 1), 884 (17, M^+ ($^{35}Cl_2$ + $^{37}Cl_2$)), 885 (13, M^+ ($^{35}Cl_2$ + $^{37}Cl_2$) + 1). Anal. Calcd for $C_{48}H_{44}Cl_4N_4O_4$: C, 65.31; H, 5.02; N, 6.35. Found: C, 65.14; H, 5.04; N, 6.30.

Compound 6b (Method A). This compound was prepared from the reaction between 1,3-bis(aminomethyl)benzene and 2,6-bis(bromomethyl)-4-bromophenol.[10] Column chromatography of the resultant material on silica gel (*n*-hexane−C_6H_6, 2/1, v/v) followed by recrystallization from CH_2Cl_2−CH_3CN afforded a white powder (2.5%): mp > 341 °C dec; ^{1}H NMR δ 10.69 (s, 4H), 8.75 (s, 2H), 7.13 (t, J = 8 Hz, 2H), 7.02 (d, J = 8 Hz, 4H), 7.15−7.11 (m, 8H), 4.36 (d, J = 14 Hz, 4H), 4.28 (d, J = 13 Hz, 4H), 4.11 (d, J = 13 Hz, 4H), 3.11 (d, J = 14 Hz, 4H), 3.06 (d, J = 13 Hz, 4H), 2.62 (d, J = 13 Hz, 4H); MS (FAB) *m/z* 1056 (0.2, M^+ ($^{79}Br_4$), 1057 (0.4, M^+ ($^{79}Br_4$) + 1), 1059 (1.1, M^+ ($^{79}Br_3$ + ^{81}Br) + 1), 1060 (1.2, M^+ ($^{79}Br_2$ + $^{81}Br_2$)), 1061 (1.6, M^+ ($^{79}Br_2$ + $^{81}Br_2$) + 1). Anal. Calcd for $C_{48}H_{44}Br_4N_4O_4$: C, 54.36; H, 4.18; N, 5.28. Found: C, 54.28; H, 4.20 N, 5.49.

$K^+ \subset$ 7·Br^- (Method B). This compound was prepared from the reaction between 1,3-bis(aminomethyl)-2-fluorobenzene dihydrochloride and 2,6-bis(bromomethyl)pyridine. Column chromatography of the resultant material on alumina (CH_2Cl_2−MeOH, 97/3, v/v) followed by recrystallization from CH_2Cl_2−MeOH afforded colorless prisms (1.1%): mp > 226 °C dec; ^{1}H NMR δ 7.64 (t, J = 8 Hz, 4H), 7.29 (bs, 4H), 7.21 (bs, 8H), 7.09 (t, J = 8 Hz, 2H) 4.34−2.79 (m, 24H); MS (FAB) *m/z* 759 (100, [M + K]$^+$). Anal. Calcd for $C_{44}H_{42}N_8F_2KBr$: C, 62.92; H, 5.04; N, 13.34. Found: C, 62.73; H, 5.05; N, 13.28.

$K^+ \subset$ 8·Br^- (Method B). This compound was prepared by the reaction between 1,3-bis(bromomethyl)-2-fluorobenzene and 2,6-bis(aminomethyl)pyridine dihydrochloride. Column chromatography of the resultant material on alumina (CH_2Cl_2−MeOH, 97/3, v/v) followed by recrystallization from CH_2Cl_2−MeOH afforded colorless prisms (0.8%): mp > 222.9 °C dec; ^{1}H NMR δ 7.65 (t, J = 8 Hz, 2H), 7.37−7.31 (m, 8H), 7.22 (d, J = 8 Hz, 4H), 7.13 (t, J = 7 Hz, 4H), 4.20 (d, J = 12 Hz, 4H), 3.93 (d, J = 14 Hz, 4H), 3.85 (d, J = 12 Hz, 4H), 3.33 (d, J = 14 Hz, 4H), 2.92 (d, J = 12 Hz, 4H), 2.78 (d, J = 12 Hz, 4H); MS (FAB) *m/z* 793 (100, [M + K]$^+$). Anal. Calcd for $C_{46}H_{42}N_6F_4KBr \cdot {}^5/_2H_2O$: C, 60.13; H, 5.16; N, 9.15. Found: C, 60.02; H, 5.06; N, 9.14.

Compound 9 (Method A). This compound was prepared by the reaction between 1,3-bis(aminomethyl)cyclohexane and 1,3-bis(bromomethyl)benzene. Column chromatography of the resultant material on alumina (CH_2Cl_2) followed by recrystallization from benzene afforded a white powder (2.4%): mp > 374 °C dec; ^{1}H NMR δ 8.51, 7.87, 7.72 (s, 4H), 7.21−6.89 (m, 12H), 4.46−1.93 (m, 24H), 1.75 to −0.08 (m, 20H); MS (FAB) *m/z* 692 (24, M^+). Anal. Calcd for $C_{48}H_{60}N_4 \cdot {}^1/_2C_6H_6$: C, 83.67; H, 8.67; N, 7.65. Found: C, 83.45; H, 8.60; N, 7.54.

Compound 10 (Method A). This compound was prepared from the reaction between 1,3-bis(bromomethyl)benzene and 1,5-diaminopentane. Column chromatography of the resultant material on alumina (CH_2Cl_2) followed by recrystallization from benzene afforded colorless prisms (4.1%): mp > 347.2−347.7 °C; ^{1}H NMR δ 8.01 (s, 4H), 7.12 (t, J = 7 Hz, 4H), 7.01 (d, J = 7 Hz, 8H), 3.49 (d, J = 13 Hz, 8H), 3.38 (d, J = 13 Hz, 8H), 2.29 (t, J = 5 Hz, 8H), 1.65−1.35 (m, 12H); MS (EI) *m/z* 612 (77, M^+). Anal. Calcd for $C_{42}H_{52}N_4$: C, 82.31; H, 8.55; N, 9.14. Found: C, 82.30; H, 8.54; N, 9.04.

Compound 11 (Method B). This compound was prepared from the reaction between 1,5-diamino-3-oxapentane dihydrochloride and 1,3-bis(bromomethyl)benzene. Column chromatography of the resultant material on alumina (CH_2Cl_2−MeOH, 98/2, v/v) followed by recrystallization from CH_2Cl_2−C_6H_6 afforded colorless prisms (3.9% yield): mp > 306.8 °C dec; ^{1}H NMR δ 8.13 (s, 4H), 7.12 (t, J = 7 Hz, 4H), 7.02 (d, J = 7 Hz, 8H), 3.81 (t, J = 6 Hz, 8H), 3.62 (d, J = 13 Hz, 8H), 3.46 (d, J = 13 Hz, 8H), 2.52 (t, J = 6 Hz, 8H); MS (FAB) *m/z* 616 (8, M^+). Anal. Calcd for $C_{40}H_{48}N_4O_2$: C, 77.89; H, 7.84; N, 9.08. Found: C, 77.64; H, 7.87; N, 9.01.

$K^+ \subset$ 12·Br^- (Method B). This compound was prepared from the reaction between 1,5-diamino-3-oxapentane dihydrochloride and 1,3-bis(bromomethyl)-2-fluorobenzene. Column chromatography of the resultant material on alumina (CH_2-

(12) The dibromide was obtained from 5-methoxy-*m*-xylene by oxidation with $KMnO_4$, esterification, reduction with $LiAlH_4$, followed by bromination with PBr_3.

Cl_2−MeOH, 98/5, v/v) followed by recrystallization from CH_2Cl_2−MeOH afforded colorless granules (1.3%): mp > 362 °C dec; ^{1}H NMR (CD_2Cl_2) δ 7.29 (t, J = 7 Hz, 8H), 7.15 (t, J = 7 Hz, 4H), 4.50−2.00 (m, 32H); MS (FAB) m/z 727 (88, [M + K]$^+$). Anal. Calcd for $C_{40}H_{44}F_4N_4O_2KBr\cdot{}^1/_2H_2O$: C, 58.82; H, 5.55; N, 6.86. Found: C, 58.58; H, 5.61; N, 6.83.

$K^+ \subset$ 13·Br^- (Method B). This compound was prepared from the reaction between 1,5-diamino-3-oxapentane dihydrochloride and 2,6-bis(bromomethyl)pyridine. Column chromatography of the resultant material on alumina (CH_2Cl_2−MeOH, 98/2, v/v) followed by recrystallization from CH_2Cl_2−MeOH afforded colorless prisms (1.0%): mp > 275.5 °C dec; ^{1}H NMR δ 7.61 (t, J = 8 Hz, 4H) 7.14 (d, J = 8 Hz, 8H), 3.72 (d, J = 13 Hz, 8H), 3.57 (t, J = 5 Hz, 8H), 3.59 (d, J = 13 Hz, 8H), 2.51 (t, J = 5 Hz, 8H); MS (FAB) m/z 659 (100, [M + K]$^+$). Anal. Calcd for $C_{36}H_{44}N_8O_2KBr$: C, 58.45; H, 5.99; N, 15.15. Found: C, 58.72; H, 6.13; N, 15.26.

Compound 14 (Method A). This compound was prepared from the reaction between *N*-(2-aminoethyl)-*N*-methyl-1,2-ethanediamine and 1,3-bis(bromomethyl)benzene. Column chromatography of the resultant material on alumina (CH_2Cl_2−MeOH, 97/3, v/v) followed by recrystallization from CH_2Cl_2−MeOH afforded colorless needles (1.2%): mp > 243.5 °C dec; ^{1}H NMR δ 8.11 (s, 4H), 7.13 (t, J = 8 Hz, 4H), 7.04 (d, J = 8 Hz, 8H), 3.58 (d, J = 13 Hz, 8H), 3.42 (d, J = 13 Hz, 8H), 3.06 (t, J = 6 Hz, 8H), 2.45 (t, J = 6 Hz, 8H), 1.73 (s, 6H); MS (FAB) m/z 643 (66, [M + H]$^+$). Anal. Calcd for $C_{42}H_{54}N_6\cdot{}^1/_2H_2O$: C, 77.37; H, 8.50; N, 12.89. Found: C, 77.46; H, 8.41; N, 12.95.

Compound 16a. Synthesis and analytical property was reported previously:[7] ^{1}H NMR δ 8.51 (s, 2H), 7.95 (s, 4H), 7.18−7.16 (m, 6H), 6.59 (t, J = 7 Hz, 4H), 6.47 (d, J = 7 Hz, 8H), 4.09 (d, J = 13 Hz, 8H), 3.90 (s, 8H), 3.20 (d, J = 13 Hz, 8H).

Compound 19 (Method B). This compound was prepared from the reaction between 1,5-diaminopentane and 2,6-bis(bromomethyl)pyridine. The yellow oil thus obtained was column chromatographed on alumina (CH_2Cl_2−MeOH, 96/4, v/v). Resultant material was dissolved in minimum amount of methanol, and a small amount of $NaBPh_4$ was added. The crystals were separated and recrystallized from CH_2Cl_2−MeOH. Colorless plates (0.9%): mp 186.5−187.4 °C; ^{1}H NMR δ 9.93 (s, 1H), 7.63−7.57 (m, 3H), 7.42 (s, 8H), 7.13−7.09 (m, 6H), 7.01 (t, J = 7 Hz, 8H), 6.86 (t, J = 7 Hz, 4H), 4.10 (d, J = 14 Hz, 2H), 3.97 (d, J = 13 Hz, 2H), 3.73 (d, J = 13.1 Hz, 2H), 3.56 (d, J = 13 Hz, 2H), 3.52 (d, J = 13 Hz, 2H), 3.39 (d, J = 14 Hz, 2H), 2.98 (bs, 2H), 2.39 (bs, 2H), 2.16 (bs, 4H), 1.72 (bs, 4H), 1.68 (bs, 2H), 1.32 (m, 2H), 0.33 (m, 2H), 0.03 (m, 4H); MS (FAB) m/z 514 (100, M^+ + 1). Anal. Calcd for $C_{55}H_{64}N_7B\cdot H_2O$: C, 77.54; H, 7.81; N, 11.51. Found: C, 77.70; H, 7.78; N, 11.53.

Compound 20 (Method B). This compound was prepared from the reaction between 1,2-bis(2-aminoethoxy)ethane and 2,6-bis(bromomethyl)pyridine. After column chromatography of the resultant material on alumina (CH_2Cl_2−MeOH, 98/2, v/v), the orange oil thus obtained was added to a small amount of MeOH. A large excess of sodium tetraphenylborate was added to the solution to give a white precipitate. Recrystallization from CH_2Cl_2−MeOH afforded colorless fine needles (0.7%): mp 194.6−195.4 °C; ^{1}H NMR δ 7.60 (t, J = 8 Hz, 2H), 7.39 (s, 8H), 6.93 (t, J = 8 Hz, 12H), 6.78 (t, J = 7 Hz, 4H), 3.98 (d, J = 18 Hz, 4H), 3.74 (d, J = 18 Hz, 4H), 3.29 (t, J = 5 Hz, 4H), 2.99 (s, 4H), 2.95 (t, J = 5 Hz, 4H); MS (FAB) m/z 355 (100, [M + H]$^+$). Anal. Calcd for $C_{44}H_{47}N_4O_2B\cdot{}^1/_4H_2O$: C, 77.81; H, 7.05; N, 8.25. Found: C, 77.98; H, 6.98; N, 8.27.

Table 1. Crystallographic Data for $K^+ \subset$ 4a, 10, and 16a

compd	$K^+ \subset$ **4a**·Pic^-	**10**	**16a**
empirical formula	$C_{48}H_{44}N_{13}O_7K$	$C_{42}H_{52}N_4$	$C_{80.75}H_{81}N_6$
FW	954.06	612.90	1135.57
T (°C)	15	−180	−180
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$P2_1/n$	$C2/c$
unit cell dimensions			
a (pm)	1067.2(2)	1228.43(2)	2879.35(4)
b (pm)	1696(2)	2116.05(3)	1566.83(2)
c (pm)	1317.0(3)	1491.70(3)	2928.71(3)
β (deg)	99.40(2)	112.5150(5)	102.3832(4)
volume (pm^3)	2351×10^6	3582×10^6	12905×10^6
Z	2	4	8
D_{calc} (g·cm^{-3})	1.35	1.14	1.17
$F000$	996.00	1328.00	4860.00
μ(Mo Kα) (cm^{-1})	1.80	0.66	0.68
$2\theta_{max}$ (deg)	55.0	55.0	55.0
GOF	0.87	1.38	1.11
R/R_w	0.074/0.071	0.076/0.077	0.053/0.083

X-ray Crystallographic Analyses.[13] The main crystallographic features are shown in Table 1. All measurements were collected on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated Mo Kα radiation for $K^+ \subset$ **4a**·Pic^- and on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation for **10** and **16a**. All structures were solved by direct methods (SAPI91[14] for $K^+ \subset$ **4a**·Pic^-, SIR92[15] for **10**, and MITHRIL84[16] for **16a**) and refined by full-matrix least-squares techniques. The non-hydrogen atoms were refined anisotoropically. For $K^+ \subset$ **4a**·Pic^-, hydrogen atoms were included, but their positions were not refined, and isotopic B values were refined. For the structure of **10** and **16a**, hydrogen atoms were included but not refined. All calculations were performed using teXscan crystallographic software package of Molecular Structure Corp.

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Supporting Information Available: ^{1}H (some of ^{13}C and ^{19}F) NMR spectra of compounds **1**−**17**, **19**, and **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 111963 for $K^+ \subset$ **4a**·Pic^-, no. CCDC 136907 for **10**, and no. CCDC 136908 for **16a**. 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).

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