Syntheses of Macrocyclic Compounds Possessing Fluorine Atoms in Their Cavities: Structures and Complexation with Cations

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Novel fluorine-containing macrocyclic molecules have been synthesized in order to clarify the interaction or coordination ability of the C–F unit towards metal ions. The cage compounds **1** and **2** were prepared by direct coupling reactions between the appropriate diamines and dibromides, while bond isomers of the cage compounds were synthesized via fluorinated diaza[3.3]metacyclophanes. Complex formation with alkali metal cations, NH_4^+, and Ag^+ ions has been assessed by picrate extraction experiments. Comparison of the cation affinities of hosts **1**, **2**, and **4**, shows that the spatial arrangement of the fluorine atoms strongly affects the donor ability of the host molecules. The hexafluoro cage compound **1**, with six fluorine atoms in an octahedral geometry, exhibits relatively strong coordination ability towards K^+, NH_4^+, and Ag^+ ions, while compound **2**, with four fluorine atoms in a structure similar to that of **1** shows only poor affinity for these ions. Compound **4**, which has six fluorine atoms arranged in a quasi planar fashion, was found to show weak affinity towards NH_4^+ and Ag^+ ions. Thus, octahedrally arranged fluorine atoms evidently provide the best fit for spherical cations. Compound **1** shows characteristic ^{1}H-, ^{13}C-, and ^{19}F-NMR-spectral changes upon complexation. The crystal structure of **1** has been elucidated and compared to that of the K^+ complex. The C–F bonds are found to be slightly elongated in the K^+ complex, which is clearly indicative of coordination of the fluorine atom to K^+.

Introduction

Since Glusker's research revealed the possibility of interactions between covalently bonded fluorine atoms (C−F) and metal cations, many examples of short C−F···M^+ distances have been proven by crystallographic analyses.[1] Concurrently, theoretical studies using computational calculations have been supportive of such interactions.[2] However, very little experimental evidence for C−F···M^+ interactions is known.[3] Recent advances in this field have stemmed from the work of Plenio et al. They have reported several types of fluorine-containing crown ether and cryptand derivatives, and have shown clear evidence of CF···M^+ interactions with alkali and alkaline earth metal cations on the basis of characteristic spectral changes (^{13}C- and ^{19}F-NMR) seen upon complexation, as well as on the binding character.[4]

On the other hand, we have shown the existence of C−F···K^+ interactions in solution as well as in the crystalline state by using the fluorine-containing cage compound **1**.[5] In this system, the bridgehead nitrogen atoms do not act as donors, but six fluorine atoms coordinate to a potassium ion in an octahedral fashion. Subsequently, we began to estimate the structural effect on complexation, i.e. the spatial arrangement of fluorine atoms and/or the number of fluorine atoms in the macrocyclic system. Since we have already reported the inclusion properties of pyridine cage compounds and their bond isomers toward metal cations and organic guests,[6] we have now applied these structures to the fluorine-containing macrocyclic system. Syntheses and cation affinities of these macrocyclic compounds, as well as the spectral features of the complexes are reported.

Results and Discussion

Syntheses

The synthesis of compound **1** has been reported previously.[5] Compound **2** was prepared in a similar manner to **1** (Figure 1). Reaction of 2-fluoro-1,3-bis(bromomethyl)-benzene with 1,3-bis(aminomethyl)benzene in refluxing dioxane afforded **2** in 3.2% yield (Scheme 1). Separation of the product was easily achieved by chromatographic techniques. In this reaction, the main products were quaternary ammonium salts and polymers, and isolable macrocyclic products were cage-type compounds such as **1** and **2**. Possible bond isomers **4** (an isomer of **1**), **7**, and **9** (isomers of **2**) were not generated. This was confirmed by syntheses of all other bond isomers **4**, **7**, and **9** via the cyclophane units **12** and **14** (Figure 2).

A synthesis of the cyclophane unit **12** has been reported by Plenio et al.[4g] However, we employed an alternative

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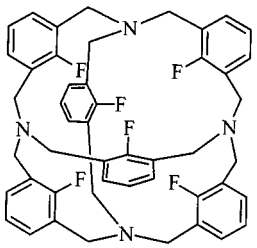

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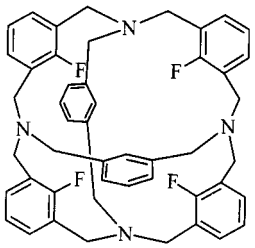

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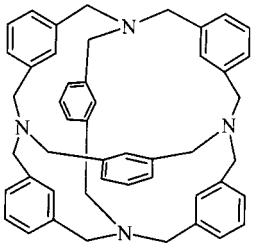

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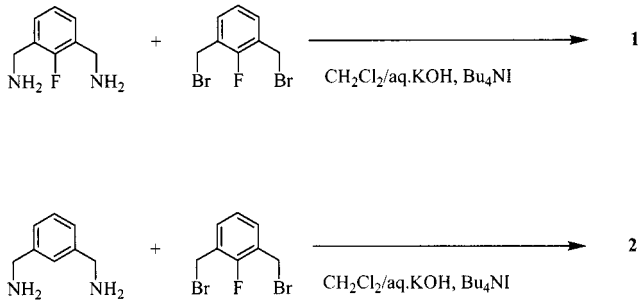
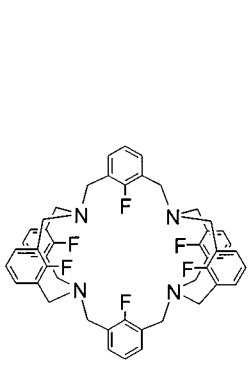
Figure 1. Structures of cage compounds **1**–**3**



Scheme 1. Synthetic scheme for compounds **1** and **2**

phenol afforded 9,18-difluoro-2,11-diaza[3.3]metacyclophane **12b** (*syn* 26.4% and *anti* 21.0%, respectively).[4g] Although the *syn* and *anti* isomers could easily be separated by preparative TLC (CH_2Cl_2/MeOH/aq. NH_3, 95:4:1), the mixture was used directly for the next cyclization step. Conformational analyses of the two isomers are currently in progress and will be published elsewhere in due course. The cyclophane **12b** was reacted with 2-fluoro-1,3-bis(bromomethyl)benzene in acetonitrile with Cs_2CO_3 as a base to give compound **4** (18.1%) together with trimeric **5** (11.6%) and tetrameric product **6** (3.3%).[6d] Compound **7** (11.7%) was obtained in a similar manner as **4**, accompanied by the trimeric product **8** (8.7%).



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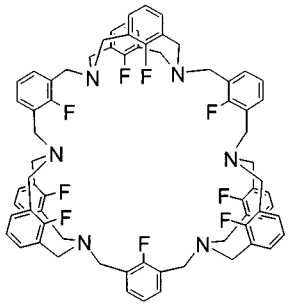

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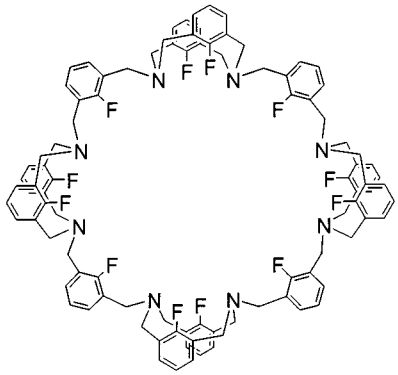

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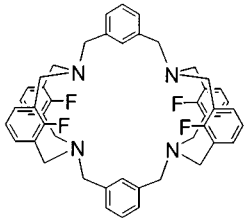

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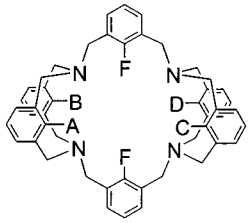


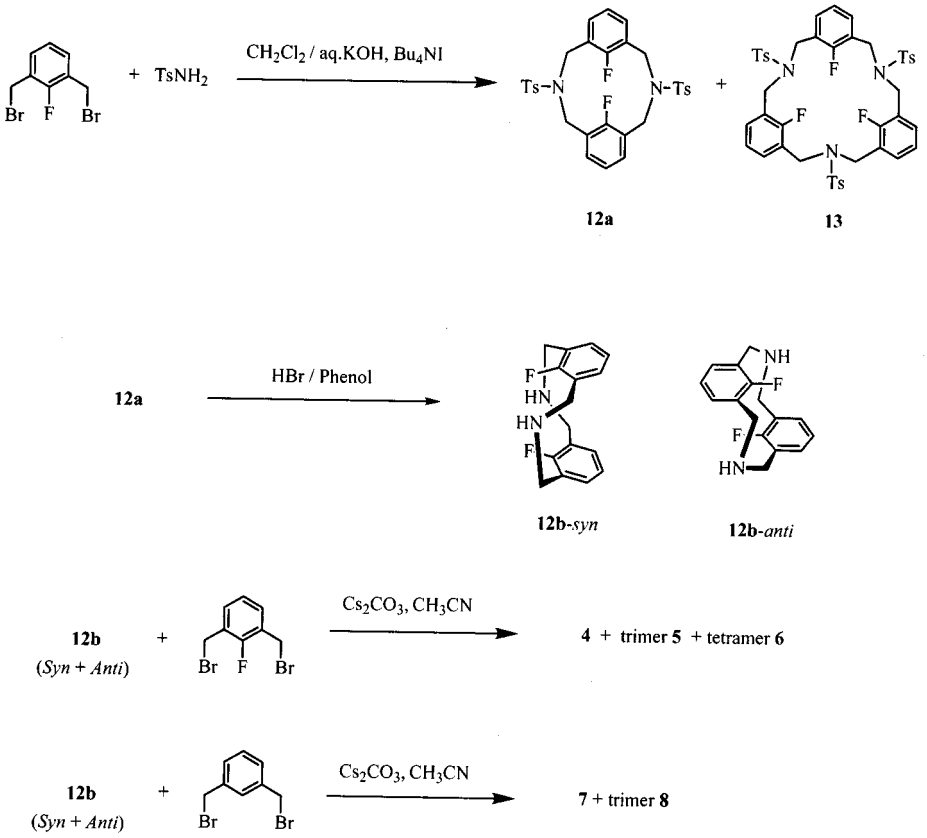
9a, 9b

	A	B	C	D
9a:	F	H	F	H
9b:	F	H	H	F

Figure 2. Structures of compounds **4**–**7** and **9**

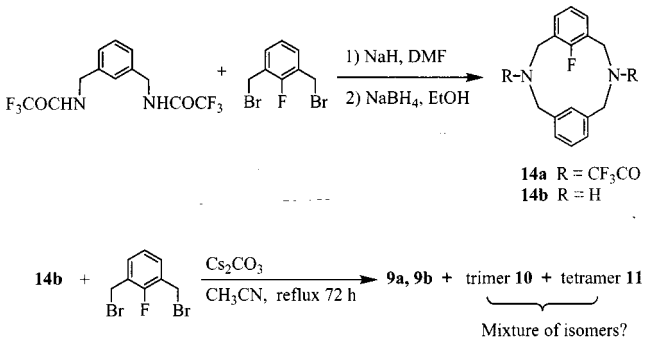
method for obtaining **12** (Scheme 2). A coupling reaction between 2-fluoro-1,3-bis(bromomethyl)benzene and *p*-toluenesulfonamide under phase-transfer conditions (CH_2Cl_2, Bu_4NI/aq. KOH) afforded **12a** (25%) along with the trimeric product **13** (3.7%).[7] Detosylation of **12a** with HBr/

Synthesis of the cyclophane unit **14** was achieved by the trifluoroacetamide method, as we have reported previously (Scheme 3).[8] Plenio et al. also employed this method in the synthesis of **14b**, which they obtained directly from the starting materials.[4g] On the other hand, we isolated the



Scheme 2. Synthetic scheme for cyclophanes **12**, **13** and macrocycles **4**–**8**

intermediate 9-fluoro-*N*,*N*′-bis(trifluoroacetyl)-2,11-diaza-[3.3]metacyclophane **14a** in 34% yield. Reductive deprotection of **14a** with $NaBH_4$ in ethanol afforded **14b** (78%). The macrocyclic compounds **9**, **10**, and **11** were obtained from a coupling reaction between **14b** and 2-fluoro-1,3-bis(bromomethyl)benzene carried out under similar conditions as the synthesis of **4**. Isomers of compounds **9**, **10**, and **11** should exist in which the fluorobenzene units reside on the same or opposite sides, as shown in Figure 2. In fact, isomers **9a** and **9b** could be separated by chromatography, but could not be identified from their NMR spectra. The ^{1}H-NMR spectral features differ considerably between the two isomers: one of them gives rise to sharp signals at room temperature, but the other exhibits a very broad band, which



Scheme 3. Synthetic scheme for cyclophanes **14a**, **b** and macrocycles **9**–**11**

does not become sharp even at 50 °C in $CDCl_3$. We could not establish whether or not the trimeric and tetrameric compounds **10** and **11** were obtained as isomeric mixtures.

Structures of Compounds 1 and 7

The structure of $K^+ \subset$ **1** and its coordination pattern has been determined previously.[5] As an extension of this work, we have to determine the structure of **1** and to compare its structure before and after the complexation. A single crystal suitable for X-ray analysis was obtained from a toluene solution of **1**. Figure 3 shows the crystal structure of **1**. One of the four nitrogen lone pairs is directed towards the exterior of the molecule (N4) and this feature is quite different from the corresponding fluorine-free compound **3**. Compound **3** has T_d symmetry, and its four nitrogen lone pairs are directed towards the center of the molecule.[6g] In the case of **1**, one of the nitrogen atoms is inverted in order to reduce the F···F repulsion. In contrast to the solid-state structure, the solution NMR spectra of **1** (^{1}H, ^{13}C, and ^{19}F) show simple patterns, implying a symmetrical structure in solution. Thus, rapid *in-out* interconversion of nitrogen and racemic motion about the bridgehead nitrogen must occur in solution at room temperature. In the ^{1}H-NMR spectrum, the signal of the benzyl proton of **1** is sharp ($W_{1/2}$ = 8.7 Hz), in contrast to the very broad signal ($W_{1/2}$ = 110 Hz) seen for the parent compound **3**. The factor that determines the line shape of the signal is the conversion rate

of the enantiomeric motion of the benzyl moiety about the bridgehead nitrogen atom.[6] The findings of the NMR analysis may be attributed to the nature of the fluorine atom; six fluorine atoms in the cavity of **1** do not slow down this motion by steric hindrance, but make it fast. In other words, the repulsive interactions of the fluorine atoms reduce the activation energy of this motion. On the other hand, all of the lone pairs in the K^+ complex of **1** are directed inwards.[5] Although the nitrogen atoms are not involved in K^+ complexation, the coordination of six fluorine atoms results in changes of the ligand structure so as to accommodate the coordination sphere of K^+. The F···F distances in **1** vary widely over the range of 3.068−5.449 Å, which is in marked contrast to the similar F···F distances (5.096−5.313 Å) found in $K^+ \subset$ **1**.

In our previous report, two structural features of the coordination of C−F to K^+ were discussed. Firstly, we addressed the matter of the F···K^+ distances, which are short (2.56−2.92 Å), whereas the N···K^+ distances are much longer (3.28−3.74 Å). Secondly, we noted that the shorter F···K^+ distances tend to make the C−F···K bond angles closer to linear. On the other hand, Plenio et al. reported that the C−F bond lengths in their ligands did not change upon complexation.[4e,4f] In our case, however, the average C−F bond length value (1.377 Å) in $K^+ \subset$ **1** is slightly longer than that in metal-free **1** (1.348 Å). This constitutes another clear and important piece of evidence for coordination of the fluorine atom to K^+. Another feature of the crystal structure is the inclusion of a solvent molecule (toluene) in the crystal lattice; this molecule resides between two concave faces of **1** (the molecular packing in the unit cell is shown in the supporting information).

Among the bond isomers of the cage compounds, structural elucidation of compound **7** was successful (Figure 4). The bridging chain ($-CH_2-N-CH_2-$) of the cyclophane moiety in **7** adopts a chair-boat conformation and the two fluorobenzene units of the cyclophane moieties are almost parallel (dihedral angles 16.15 and 20.34°, respectively). In contrast to the solid-state structure, the ^{1}H-NMR spectrum in $CDCl_3$ features sharp benzyl signals, indicating rapid chair-boat interconversion in solution. A summary of the crystallographic data and refinement details of **1** and **7** is presented in Table 1.

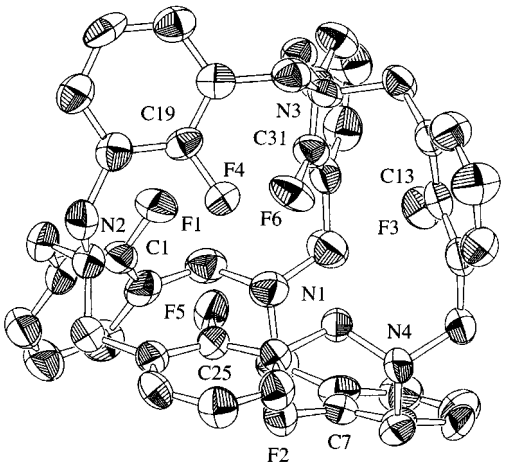


Figure 3. Crystal structure of **1** (H atoms are omitted for clarity); selected bond lengths (Å) and atomic distances (Å): C(1)−F(1) 1.351(8), C(7)−F(2) 1.366(8), C(13)−F(3) 1.355(8), C(19)−F(4) 1.336(8), C(25)−F(5) 1.350(7), C(31)−F(6) 1.331(7), F(1)−F(3) 5.449(6), F(2)−F(4) 5.371(6), F(5)−F(6) 3.068(8)

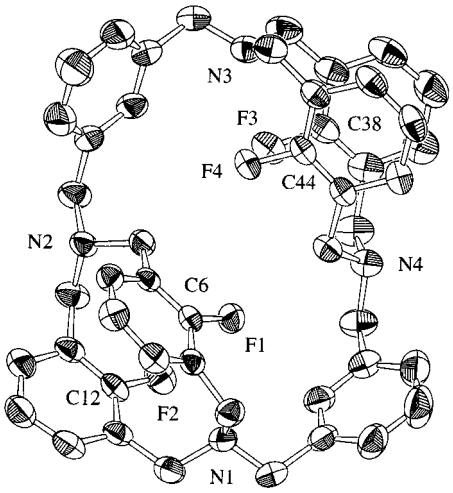


Figure 4. Crystal structure of compound **7** (H atoms are omitted for clarity); selected bond lengths (Å): C(1)−F(6) 1.361(3), C(12)−F(2) 1.362(4), C(38)−F(3) 1.368(4), C(44)−F(4) 1.364(3)

Complexation Studies

The cation selectivity of **1** and the binding constants of $M^+ \subset$ **1** (M^+ = K^+: 5.58; NH_4^+: 4.37; Ag^+: 4.57 in $CHCl_3$) were discussed in our most recent report.[5] In order to assess the effect of structure on the complexation ability, metal picrate extraction experiments were carried out using the cage compound **2** and the bond isomers **4** and **7** as ligands. The results are presented in Table 2. The fluorine-free compound **3** was used as a reference in these experiments, and it was confirmed that it does not extract metal picrates at all.[6] As reported previously, **1** was found to show strong affinities towards K^+, NH_4^+, and Ag^+. Among the alkali metal cations, it showed remarkable K^+ selectivity. On the other hand, compound **4**, a bond isomer of **1**, extracted only NH_4^+ and Ag^+ [*D* (%) NH_4^+: 13.8; Ag^+: 10.8] and did not show any affinity towards alkali metal ions. Compound **2** showed very weak affinity towards NH_4^+ and Ag^+ [*D* (%) NH_4^+: 0.53; Ag^+: 0.62]; the replacement of two F atoms in **1** by two H atoms drastically reduces the complexation ability. Complexation abilities of **2** and **7** towards alkali metal ions are negligible. The differences in cation affinities among **1**, **2**, **4**, and **7** should correspond to their geometries and the number of C−F units. While **1** can surround the spherical ions with six fluorine atoms that constitute a three-dimensional coordination site, the geometries of C−F units in **2**, **4**, and **7** can be regarded as being almost planar.

Table 1. Summary of crystallographic data and refinement details

Compound	**1**	**7**
Formula	$C_{55}H_{50}F_6N_4$	$C_{48}H_{44}F_4N_4$
Crystal color, habit	colorless, prismatic	colorless, prismatic
Crystal size (mm)	0.40 × 0.20 × 0.40	0.16 × 0.12 × 0.15
Crystal system	monoclinic	triclinic
Space group	$P2_1$ (no. 4)	$P\bar{1}$ (no. 2)
Temperature (°C)	23 ± 1	20 ± 1
a (Å)	10.243(6)	12.865(6)
b(Å)	16.488(3)	14.667(7)
c(Å)	13.679(1)	11.808(7)
α (°)	–	102.49(5)
β (°)	100.84(1)	109.68(4)
γ (°)	–	67.87(4)
V (Å^3)	2268(1)	1933(1)
Z	2	2
D_{calcd} (g cm^{-3})	1.289	1.293
F(000)	924.00	792.00
μ (cm^{-1})	0.93(Mo)	0.89(Mo)
$2\theta_{max}$ (°)	55.0(Mo)	55.0(Mo)
No. of reflections:		
Measured	9299	7877
Independent	5397	7477
R_{int}	0.320	0.039
No. of observations [$I > 3.00\ \sigma(I)$]	2154	3929
No. of parameters	586	681
Reflection/ parameterratio	3.68	5.77
R	0.040	0.046
R_w	0.039	0.042
S	0.67	1.87
Max. Δ/σ	0.21	0.18
Max. Δρ (e^- nm^{-3})	−0.18	−0.21

The NH_4^+ and Ag^+ complexes of **1** could be isolated as crystalline materials. Addition of CF_3SO_3Ag to a solution of **1** in C_6D_6 resulted in the precipitation of $Ag^+ \subset$ **1** as colorless fine crystals. Elemental analysis of the crystals gave a satisfactory result, which corresponded to the composition of a 1:1 complex, $Ag^+ \subset$ **1**·$CF_3SO_3^-$·H_2O. The FAB mass spectrum of $Ag^+ \subset$ **1** featured two relatively strong peaks at 895 [M + ^{107}Ag] and 897 [M + ^{109}Ag]. The complexes $NH_4^+ \subset$ **1**·X^- (X = Pic, Br, BF_4) were prepared by mixing **1** and the corresponding NH_4^+ salts in a mixture of CH_2Cl_2 and MeOH. Attempts to elucidate the crystal structure of $NH_4^+ \subset$ **1** are currently in progress.

Spectral Features Accompanying Complexation

Besides the extraction experiments, the specific changes in the spectra of **1** accompanying complexation were also studied. Addition of CF_3SO_3Ag to a $CDCl_3$ solution of **1** resulted in a downfield shift (ca. 0.3 ppm) of all the signals in its ^{1}H-NMR spectrum. The reference compound **3** was similarly treated with CF_3SO_3Ag, but in this case no spectral changes were observed. Again, it is shown that the nitrogen atoms do not participate in the complexation of this macrocyclic system, and that $Ag^+\cdots\pi$ interaction does not occur. NH_4^+ complexation could be observed in a mixture of $CD_3CN/CDCl_3$ using ammonium picrate. In the absence of **1**, the NH_4^+ proton signal appeared at δ = 6.38 as a broad singlet. Upon addition of **1**, the signal was shifted to δ = 5.28 and was split into a triplet (J = 53.5 Hz). This phenomenon shows that the intermolecular proton exchange of NH_4^+ is sufficiently suppressed by the inclusion. Since $Ag^+ \subset$ **1** was found to dissociate in a mixture of $CD_3CN/CDCl_3$, the ^{1}H-, ^{13}C-, and ^{19}F-NMR-spectral data of the complexes were measured in $CDCl_3$. The results are presented in Table 3 along with data for the K^+ complex. In the ^{1}H-NMR spectra, the methylene proton signal of each complex is shifted to lower field (Δδ ≈ 0.28 ppm). The shifts in the C−F carbon signals in the ^{13}C-NMR spectra are small (Δδ ≈ 1 ppm), while the $^1J_{C-F}$ coupling constants are significantly reduced (by ca. 12 Hz). The ^{19}F-NMR spectra show high-field shifts of the signals of fluorine nuclei (Δδ ≈ 15.8 ppm). These spectral features are in accord with those reported by Plenio et al.[4] In addition to these phenomena, remarkable changes in the signal widths were observed. Although the ^{19}F signal of metal-free **1** is very broad ($W_{1/2}$ = 661 Hz), the signal becomes sharp after complexation ($W_{1/2}$ = $K^+\subset$ **1**: 16 Hz; $NH_4^+\subset$ **1**: 17 Hz; $Ag^+\subset$ **1**: 83 Hz). Upon complexation, the F atoms are rearranged so as to surround the cation species. Thus, there is an averaging of the positions of the F atoms, which results in a sharpening of the ^{19}F signal. Moreover, in the ^{1}H-NMR spectra, the methylene signal ($W_{1/2}$ = 8.7 Hz) becomes sharp ($W_{1/2}$ = $K^+ \subset$ **1**: 2.7 Hz; $NH_4^+ \subset$ **1**: 4.6 Hz) following complexation, except in the case of the Ag^+ complex (11.1 Hz).

Table 2. Liquid-liquid extraction of alkali metal picrates using compounds **1**, **2**, **4**, and **7** as ligands

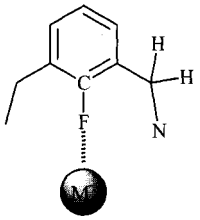
Compound	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+	Ag^+
1[a]	0.06	0.17	22.7	1.9	0.1	112	103.2
2	0	0	0	0	0	0.53	0.62
4	0	0	0	0	0	13.8	10.8
7	0	0	0	0	0	–	–

[a] Data from ref.[5]; the conditions are described in the Experimental Section.

Conclusion

Recent research has made clear the existence of C−F···cation interactions, establishing fluorine as a new member of the donor atoms in host-guest chemistry. In this study, it has been shown that fluorine acts as an effective donor atom towards cations, and that this interaction becomes detectable with the suitable design of host molecules. The geometry of C−F units in macrocyclic systems has a great effect on the strength of the complexation ability, and it is very important with regard to the detection of C−F···cation interactions. Comparison of the molecular structures of cation-free **1** and $K^+ \subset$ **1** gave evidence for the coordination of F atoms to the potassium ion. Characteristic changes in the spectra of **1** upon complexation with cations have been observed, and these features are useful tools for further investigation of the C−F···cation interaction.

Table 3. ^{1}H-, ^{19}F-NMR shifts and ^{13}C coupling constants of $M^+ \subset$ **1** in $CDCl_3$; * shift (ppm) from $CFCl_3$.



metal	^{1}H δ-CH_2- (ppm)	^{13}C $^1J_{C\text{-}F}$ (Hz)	^{19}F δ F (ppm) *
metal free [a]	3.49	260.5	-110.50
K^+ [a]	3.65	247.8	-126.26
NH_4^+	3.68	247.8	-122.96
Ag^+	3.77	249.8	-118.74

[a] Data from ref.[5]

Experimental Section

Melting points: Yanaco MP-500D apparatus, under Ar in sealed tubes; uncorrected values. − NMR: Bruker DPX-400 (400 MHz for ^{1}H and 100.6 MHz for ^{13}C), JEOL GSX 270 (270 MHz for ^{1}H and 67.9 MHz for ^{13}C), and Bruker DMX-600 (564.7 MHz for ^{19}F). − UV/Vis: Shimadzu UV-2200. − IR: JASCO IR-700 (KBr) and Nicolet Magna 560 (CCl_4). − FAB and EI MS: JEOL JMS-SX/SX102A. − Elemental analyses: Service Centre for the Elementary Analysis of Organic Compounds affiliated to the Faculty of Science, Kyushu University. − All solvents and reagents were of reagent quality and were used without further purification.

Liquid−Liquid Extraction: Water-saturated chloroform solutions of the ligands (1.0×10^{-3} M, 5 mL) and aqueous metal salt solutions (0.10 M in LiCl to CsCl, NH_4Cl, and $AgNO_3$ containing 1.01×10^{-3} M of lithium picrate, 5 mL) were introduced into vials, which were Teflon-sealed and the contents were stirred for 15 h at 25 ± 0.1°C. A prolonged stirring time led to identical results. The resulting mixtures were allowed to stand for 30 min. at 25 ± 0.1°C and then centrifuged. The organic phases were carefully withdrawn, and the concentrations of the picrates were determined spectrophotometrically at 374 nm ($\varepsilon = 1.86 \times 10^4$). The distribution ratio, D(%), was calculated using the following equation:

$$D\ (\%) = [Pic^-]_{org}/([Pic^-]_i - [Pic^-]_{org}) \times 100$$

Here, $[Pic^-]_i$ is the initial concentration of picrate in the aqueous phase and $[Pic^-]_{org}$ is the observed concentration of picrate in the organic phase.

Compound 1: The synthetic procedure has been reported previously.[5]

The Complex $Ag^+ \subset$ 1·$CF_3SO_3^-$: M.p. > 170.9°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.30 [t, ^3J (H,H) = 6 Hz, 12 H, ArH], 7.05 [t, ^3J (H,H) = 8 Hz, 6 H, ArH], 3.77 (s, 24 H, CH_2). − ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 161.40, 158.92 [d, ^1J (C,F) = 249.8 Hz], 132.46 (s), 126.45 (s), 123.24 (s), 55.83 (s). − ^{19}F NMR (564.7 MHz, $CDCl_3$, $CFCl_3$): δ = −118.74 (s). − FAB MS: *m/z* (%) = 895 (53) [$M^+ + {}^{107}Ag^+$], 897 (53) [$M^+ + {}^{109}Ag^+$]. − $C_{48}H_{42}N_4F_6{\cdot}CF_3SO_3Ag{\cdot}H_2O$ (1063.8): calcd. C 55.32, H 4.17, N 5.27; found C 55.46, H 4.22, N 5.17.

The Complex $NH_4^+ \subset$ 1·Br^-: A mixture of **1** (48.7 mg, 0.062 mmol) and NH_4Br (100 mg, 1.02 mmol) was stirred for 24 h at room temperature in CH_2Cl_2/CH_3OH (1:1, 4 mL). After evaporation of the solvents, the residue was washed with water and then dried. Recrystallization of the resulting powder from CH_2Cl_2/C_6H_6 afforded colorless needles (50.2 mg, 86.4%), m.p. > 267.2°C (dec.). − ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.25 [d, ^3J (H,H) = 7.5 Hz, 12 H, ArH], 7.05 [t, ^3J (H,H) = 7.5 Hz, 6 H, ArH], 5.24 [t, ^1J (N,H) = 53.5 Hz, 4 H, NH_4^+], 3.68 (s, 24 H, CH_2). − ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 161.01, 158.55 [d, ^1J (C,F) = 247.8 Hz], 131.93 (s), 126.56 (s), 123.96 (s), 56.00 (s). − ^{19}F NMR (565 MHz, $CDCl_3$, $CFCl_3$): δ = −122.96 (s). − FAB MS: *m/z* (%) = 806 (50) [$M^+ + NH_4^+$]. − $C_{48}H_{42}N_4F_6{\cdot}NH_4Br{\cdot}3H_2O$ (940.9): calcd. C 61.28, H 5.68, N 7.30; found C 61.50, H 5.85, N 7.40.

Compound 2: To a refluxing solution of 1,3-bis(aminomethyl)benzene (2.06 g, 15.1 mmol) in dioxane (300 mL), a solution of 1,3-bis(bromomethyl)-2-fluorobenzene (2.34 g, 8.3 mmol) in dioxane (140 mL) was added over a period of 2.5 h. Refluxing was continued for a further 8 h, then the reaction mixture was filtered and the organic layer was concentrated in vacuo. The residue obtained was chromatographed on alumina using benzene as eluent. The white powder thus obtained was recrystallized from CH_2Cl_2/C_6H_6. Colorless prisms (49.2 mg, 3.2%), m.p. 397.9°C (dec.). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.41 (s, 2 H, ArH), 7.16−7.04 (m, 14 H, ArH), 6.88 [t, ^3J (H,H) = 7.5 Hz, 4 H, ArH], 4.21, 2.97 [dd, ^2J (H,H) = 13 Hz, 8 H, CH_2], 4.17, 2.66 [dd, ^2J (H,H) = 12 Hz, 8 H, CH_2], 4.02, 2.54 [dd, ^2J (H,H) = 12 Hz, 8 H, CH_2]. − FAB MS: *m/z* (%) = 752 (40) [M^+]. − $C_{48}H_{44}N_4F_4$ (752.9): calcd. C 76.57, H 5.89, N 7.44; found C 76.31, H 5.99, N 7.25.

9,18-Difluoro-*N*,*N*′-ditosyl-2,11-diaza[3.3]metacyclophane (12a): A mixture of *p*-toluenesulfonamide (1.24 g, 7.2 mmol), nBu_4NI (0.70 g, 1.9 mmol), CH_2Cl_2 (300 mL), and aq. 3 N KOH (50 mL) was heated under reflux with vigorous stirring. A solution of 2-fluoro-1,3-bis(bromomethyl)benzene (2.05 g, 7.3 mmol) in 120 mL of CH_2Cl_2 was then added to the mixture over a period of 3 h and heating was continued for a further 8 h. The organic layer was separated and the solvent was removed under reduced pressure. The residual material was washed with MeOH and the resulting powder was recrystallized from CH_2Cl_2/AcOEt to give a white powder (680 mg, 32%); m.p. 284.2−284.8°C. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.78 [d, ^3J(H,H) = 8 Hz, 4 H, ArH], 7.38 [d, ^3J(H,H) = 8 Hz, 4 H, ArH], 7.20−7.14 (m, 4 H, ArH), 6.77 [t, ^3J(H,H) = 8 Hz, 2 H, ArH], 4.71, 4.09 [dd, ^3J(H,H) = 14 Hz, 8 H, CH_2], 2.48 (s, 6 H, CH_3). − FAB MS: *m/z* (%) = 583 (10) [M^+ + 1]. An analytical sample was recrystallized from CH_2Cl_2/C_6H_6. − $C_{30}H_{28}N_2F_2O_4S_2$ (582.7): calcd. C 61.84, H 4.84, N 4.81; found C 61.83, H 4.90, N 4.80.

9,18,27-Trifluoro-*N*,*N*′,*N*″-tritosyl-2,11,20-triaza[3.3.3]-metacyclophane (13): Concentration of the mother liquor obtained in the recrystallization of **12a** afforded colorless granules (78.6 mg, 3.7%), m.p. 252−253°C. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.68 [d, ^3J(H,H) = 8 Hz, 6 H, ArH], 7.28 [d, ^3J(H,H) = 8 Hz, 6 H, ArH], 7.13 (m, 6 H, ArH), 6.93 [t, ^3J(H,H) = 8 Hz, 3 H, ArH], 4.24 (s, 12 H, CH_2), 2.43 (s, 9 H, CH_3). − FAB MS: *m/z* (%) = 874 (7) [M^+ + 1]. An analytical sample was recrystallized from ben-

zene. − $C_{45}H_{42}N_3F_3O_6S_3 \cdot 3/2C_6H_6$ (991.2): calcd. C 65.43, H 5.19, N 4.24; found C 65.47, H 5.19, N 4.15.

9,18-Difluoro-2,11-diaza[3.3]metacyclophane (12b): A mixture of compound **12a** (1.02 g, 1.75 mmol), phenol (5.06 g, 53.8 mmol), and 47% HBr (50 mL) was heated at 130°C for 4 h. After removal of the excess phenol by steam distillation, 6 N HCl (20 mL) was added to the residue and the resulting mixture was washed with diethyl ether. The aqueous phase was treated with aq. KOH and extracted with diethyl ether. The extracted material was purified by preparative TLC (CH_2Cl_2/MeOH/aq. NH_3, 95:4:1).

syn-**12b:** 126 mg (26.4%), m.p. 184.4−185.2°C (ref.[4g] 170−174°C). − EI MS: *m*/*z* (%) = 274 (100) [M^+]. An analytical sample was recrystallized from CH_2Cl_2/CH_3CN. − $C_{16}H_{16}N_2F_2$ (274.3): calcd. C 70.02, H 5.88, N 10.21; found C 70.19, H 5.95, N 10.15. − IR (KBr): $\tilde{\nu}$ = 3370, 3272 (ν_{NH}); (CCl_4): $\tilde{\nu}$ = 3402 cm^{-1}.

anti-**12b:** 100 mg (21.0%), m.p. 178.2−179.5°C (ref.[4g] 186°C). − EI MS: *m*/*z* (%) = 274 (100) [M^+]. An analytical sample was recrystallized from CH_2Cl_2/CH_3CN. − $C_{16}H_{16}N_2F_2$ (274.3): calcd. C 70.02, H 5.88, N 10.21; found C 70.00, H 5.87, N 10.15. − IR (KBr): $\tilde{\nu}$ = 3354, 3250 (ν_{NH}); (CCl_4): $\tilde{\nu}$ = 3375 cm^{-1}. All other spectral data (^{1}H-, ^{13}C-, and ^{19}F-NMR) were in complete agreement with that reported previously.[4g]

9-Fluoro-*N*,*N*′-bis(trifluoroacetyl)-2,11-diaza[3.3]metacyclophane (14a): *N*,*N*′-Bis(trifluoroacetyl)-*m*-xylylenediamine (5.00 g, 15.2 mmol) was slowly added to a suspension of NaH (1.60 g, 60% in mineral oil) in dry DMF (400 mL) and the mixture was stirred at 50°C. A solution of 1,3-bis(bromomethyl)-2-fluorobenzene (4.40 g, 15.6 mmol) in 100 mL of dry DMF was then added over a period of 4 h and stirring was continued for a further 4 h. The solvent was subsequently removed in vacuo and the resulting material was subjected to column chromatography on silica gel using CH_2Cl_2/MeOH (98:2) as eluent. Recrystallization of the product from ethanol afforded colorless granules (2.30 g, 34%), m.p. 151.4−152.7°C. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.06−6.76 (m, 7 H, ArH), 5.20−4.25 (m, 8 H, CH_2). − $C_{20}H_{15}N_2O_2F_7$ (448.3): calcd. C 53.58, H 3.37, N 6.25; found C 53.46, H 3.43, N 6.08.

9-Fluoro-2,11-diaza[3.3]metacyclophane (14b): To a solution of **14a** (1.02 g, 2.28 mmol) in 50 mL of ethanol was added $NaBH_4$ (1.04 g, 27.4 mmol) at 40°C and the mixture was heated under reflux for 2 h. After removal of the solvent, the resulting white material was suspended in 100 mL of water. This suspension was extracted with CH_2Cl_2 (3 × 30 mL) and the combined extracts were dried over K_2CO_3. Removal of the solvent afforded a white solid, which was recrystallized from hexane to give colorless needles (454 mg, 78%); m.p. 118.8−121.8°C (ref.[4g] 126°C). − $C_{16}H_{17}N_2F$ (256.3): calcd. C 74.98, H 6.68, N 10.93; found C 75.08, H 6.71, N 10.72. − ^{1}H-NMR and mass-spectral data were consistent with those reported previously.[4g]

Compounds 4, 5, and 6: A mixture of **12b** (102 mg, 0.37 mmol), Cs_2CO_3 (552 mg, 1.7 mmol), and water (5 mL) in acetonitrile (400 mL) was heated under reflux with stirring. After 30 min., a solution of 2-fluoro-1,3-bis(bromomethyl)benzene (106 mg, 0.37 mmol) in acetonitrile (20 mL) was added in one portion and heating was continued for 4 days. The solvent was then removed under reduced pressure and the residue was extracted with CH_2Cl_2. The combined extracts were concentrated and the resulting material was subjected to preparative TLC (CH_2Cl_2/MeOH, 98:2).

Compound 4: Colorless fine needles (26.5 mg, 18.1%, recrystallized from CH_2Cl_2/CH_3CN), m.p. 332.3−334.1°C. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.35 [t, ^3J(H,H) = 7 Hz, 4 H, ArH], 7.10 [t, ^3J(H,H) = 8 Hz, 2 H, ArH], 6.62 (br. s, 8 H, ArH), 6.42 [t, ^3J(H,H) = 8 Hz, 4 H, ArH], 4.05, 3.38 [A_2X_2, ^2J(H,H) = 13 Hz, 16 H, CH_2], 4.03 (s, 8 H, CH_2). − FAB MS: *m*/*z* (%) = 789 (8) [M^+ + 1]. − $C_{48}H_{42}N_4F_6$ (788.9): calcd. C 73.08, H 5.37, N 7.10; found C 73.03, H 5.45, N 7.06.

Compound 5: White powder (17.0 mg, 11.6%, recrystallized from CH_2ClCH_2Cl), m.p. 324−326°C (dec.). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.36 [t, ^3J(H,H) = 7 Hz, 6 H, ArH], 7.13 [t, ^3J(H,H) = 7 Hz, 3 H, ArH], 6.66−6.62 (m, 12 H, ArH), 6.32 [t, ^3J(H,H) = 8 Hz, 6 H, ArH], 3.96 (s, 12 H, CH_2), 3.93, 3.59 [A_2B_2, ^2J(H,H) = 13 Hz, 24 H, CH_2]. − FAB MS: *m*/*z* (%) = 1184 (9) [M^+ + 1]. − $C_{72}H_{63}N_6F_9 \cdot CH_2ClCH_2Cl$ (1282.3): calcd. C 69.32, H 5.27, N 6.55; found C 69.26, H 5.31, N 6.57. The quantity of solvent retained in the analytical sample was confirmed by analysis of the ^{1}H-NMR spectrum.

Compound 6: White powder (4.9 mg, 3.3%, recrystallized from CH_2Cl_2/CH_3CN), m.p. 296.7−298.3°C. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.53 [t, ^3J(H,H) = 7 Hz, 8 H, ArH], 7.20 [t, ^3J(H,H) = 7 Hz, 4 H, ArH], 6.71−6.68 (m, 16 H, ArH), 6.35 [t, ^3J(H,H) = 7 Hz, 8 H, ArH], 3.98 (s, 16 H, CH_2), 3.91, 3.56 [A_2B_2, ^2J(H,H) = 13 Hz, 32 H, CH_2]. − FAB MS: *m*/*z* (%) = 1578 (10) [M^+ + 1]. − $C_{96}H_{84}N_8F_{12}$ (1577.8): calcd. C 73.08, H 5.37, N 7.10; found C 72.82, H 5.42, N 7.03.

Compounds 7 and 8: A solution of **12b** (98.7 mg, 0.35 mmol), Cs_2CO_3 (402.6 mg, 1.24 mmol), and water (4 mL) in acetonitrile (280 mL) was heated under reflux with stirring. After 30 min., a solution of 1,3-bis(bromomethyl)benzene (97.1 mg, 0.37 mmol) in acetonitrile (20 mL) was added in one portion and the mixture was heated for 3 days. The solvent was then removed under reduced pressure and the residue was extracted with CH_2Cl_2. The combined extracts were concentrated and subjected to preparative TLC (SiO_2, CH_2Cl_2/MeOH, 98:2).

Compound 7: Colorless prisms (16.3 mg, 11.7%, recrystallized from CH_2Cl_2/CH_3CN), m.p. 266.1−267.2°C. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.12 (s, 2 H, ArH), 7.31−7.29 (m, 6 H, ArH), 6.59 (br. s, 8 H, ArH), 6.42 [t, ^3J(H,H) = 8 Hz, 4 H, ArH], 4.02, 3.40 [A_2X_2, ^2J(H,H) = 14 Hz, 16 H, CH_2], 3.89 (s, 8 H, CH_2). − FAB MS: *m*/*z* (%) = 752 (40) [M^+], 753 (55) [M^+ + 1]. − $C_{48}H_{44}N_4F_4$ (752.9): calcd. C 76.57, H 5.89, N 7.44; found C 76.46, H 5.93, N 7.45.

Compound 8: White powder (12.0 mg, 8.7%, recrystallized from hexane/CH_2Cl_2), m.p. 325.1−326.1°C. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.21 (s, 3 H, ArH), 7.39−7.23 (m, 9 H, ArH), 6.99−6.96 (m, 12 H, ArH), 6.55 [t, ^3J(H,H) = 7 Hz, 6 H, ArH], 3.98 (s, 12 H, CH_2), 3.90, 3.69 [A_2B_2, ^2J(H,H) = 13 Hz, 24 H, CH_2]. − FAB MS: *m*/*z* (%) = 1128 (0.24) [M^+], 1129 (0.42) [M^+ + 1]. − $C_{72}H_{66}N_6F_6$ (1129.4): calcd. C 76.57, H 5.89, N 7.44; found C 76.55, H 5.89, N 7.36.

Compounds 9, 10, and 11: A solution of **14b** (202 mg, 0.788 mmol), Cs_2CO_3 (513 mg, 1.57 mmol), 1,3-bis(bromomethyl)-2-fluorobenzene (226 mg, 0.802 mmol), and 10 mL of water in 300 mL of CH_3CN was heated under reflux for 3 days. After removal of the solvent, the residual white powder was subjected to preparative TLC (silica gel, CH_2Cl_2/acetone, 95:5).

Compound 9a or 9b: Colorless needles (86 mg, 29.0%, recrystallized from CH_2Cl_2/CH_3CN), m.p. 299.9−300.5°C. − ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 7.50 (br. s, 2 H, ArH), 7.28 (s, 4 H, ArH), 7.06 [t, ^3J(H,H) = 8 Hz, 2 H, ArH], 6.64 (br. s, 4 H, ArH), 6.35 [t, ^3J(H,H) = 8 Hz, 2 H, ArH], 6.14 [t, ^3J(H,H) = 8 Hz, 2 H, ArH], 5.85 (br. s, 4 H, ArH), 4.6−2.8 (br. m, 24 H, CH_2). − FAB MS: *m*/*z* (%) = 753 (88) [M + H^+]. − $C_{48}H_{44}N_4F_4 \cdot 1/6(CH_2Cl_2 \cdot CH_3CN)$ (773.9): calcd. C 75.27, H 5.84, N 7.54; found C 75.52, H 5.90, N

7.78. The quantities of the solvents retained in the analytical sample were confirmed by analysis of the ^{1}H-NMR spectrum.

Compound 9a or 9b: Colorless prisms (63 mg, 21.3%, recrystallized from CH_2Cl_2/C_6H_6), m.p. 298.2−298.6°C. − ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 7.55 (s, 2 H, ArH), 7.35 (br. s, 4 H, ArH), 7.11 [t, ^3J(H,H) = 8 Hz, 2 H, ArH], 6.65−6.53 (m, 10 H, ArH), 6.38 [t, ^3J(H,H) = 8 Hz, 2 H, ArH], 4.04 (s, 8 H, CH_2), 3.98, 3.29 [A_2X_2, ^2J(H,H) = 9 Hz, 8 H, CH_2], 3.70 (br. s, 8 H, CH_2). − FAB MS: *m*/*z* (%) = 753 (68) [M + H$^+$]. − $C_{48}H_{44}N_4F_4{\cdot}C_6H_6{\cdot}1/2CH_2Cl_2$ (873.5): calcd. C 76.98, H 6.00, N 6.63; found C 77.05, H 6.02, N 6.62. The quantities of solvents retained in the analytical sample were confirmed by analysis of the ^{1}H-NMR spectrum.

Compound 10a or 10b (mixture of two isomers?): Colorless powder (45 mg, 15.2%, recrystallized from CH_2ClCH_2Cl), m.p. 286.7−287.9°C. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.98 (s, 6 H, ArH), 7.83 (s, 3 H, ArH), 7.46 (m, 3 H, ArH), 6.67 [t, ^3J(H,H) = 8 Hz, 3 H, ArH], 6.60 [t, ^3J(H,H) = 7 Hz, 6 H, ArH], 6.48 [d, ^3J(H,H) = 7 Hz, 6 H, ArH], 6.33 [t, ^3J(H,H) = 7 Hz, 3 H, ArH], 4.33, 3.97, 3.40, 3.25 (m, 24 H, CH_2), 3.96 (s, 12 H, CH_2). − FAB MS: *m*/*z* (%) = 1129 (6) [M + H$^+$]. − $C_{72}H_{66}N_6F_6{\cdot}2/3\ CH_2ClCH_2Cl$ (1195.3): calcd. C 73.69, H 5.79, N 7.03; found C 73.68, H 5.82, N 7.00. The quantity of solvent retained in the analytical sample was confirmed by analysis of the ^{1}H-NMR spectrum.

Compounds 11a−d (mixture of four isomers?): Colorless powder (47 mg, 15.9%, recrystallized from CH_2Cl_2/CH_3CN), m.p. 201.5−217.8°C. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.66 [t, ^3J(H,H) = 7 Hz, 8 H, ArH], 7.59 (s, 4 H, ArH), 7.25 [t, ^3J(H,H) = 7 Hz, 4H, ArH], 6.68−6.57 (m, 20 H, ArH), 6.35 [t, ^3J(H,H) = 7 Hz, 4 H, ArH], 4.08, 3.35 [A_2X_2, ^2J(H,H) = 12 Hz, 16 H, CH_2), 3.96 (s, 16 H, CH_2), 3.71, 3.61 [A_2B_2, ^2J(H,H) = 14 Hz, 16 H, CH_2]. − FAB MS: *m*/*z* = 1505 (0.5) [M + H$^+$]. − $C_{96}H_{88}N_8F_8$ (1505.8): calcd. C 76.57, H 5.89, N 7.44; found C 76.51, H 5.98, N 7.25.

X-ray Crystallographic Studies:[9] All measurements were made with a Rigaku AFC7R diffractometer using graphite-monochromated Mo-K_α radiation and a rotating anode generator. The structure was solved by direct methods (SIR-92) and expanded using Fourier techniques (DIRDIF-94). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXscan crystallographic software package of the Molecular Structure Corporation.

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[9] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-103114 (compound **1**) and -112389 (compound **7**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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