# Supplementary data

**Table S1. Cyclization Yields of *trans*-BCMB24C8 (2) in MeCN at reflux.**

| [**8**]$_o$[a] (mM) | [$K_2CO_3$]$_o$ (mM) | [$KPF_6$]$_o$ (mM) | Yield (%) | | | |
|---|---|---|---|---|---|---|
| | | | **2** | **9** | **2/9** | Total |
| 170 | 509 | 84.5 | 32 | 15 | 2.1 | 47 |
| 62.8 | 314 | 94.0 | 32 | 27 | 1.2 | 59 |
| 22.6 | 67.8 | 11.3 | 44 | 36 | 1.2 | 79 |
| 25.5 | 76.7 | 12.6 | 42 | 35 | 1.2 | 77 |

[a] The subscript "o" indicates the original concentration.

**TABLE S2. Complexation of *cis*-BCMDB24C8 (1) with Dibenzylammonium Hexafluorophosphate (10) in $CD_3CN$: $CDCl_3$ (2:3) at 22±1 °C.[a]**

| [**1**]$_0$ (mM) | [**10**]$_0$ (mM) | **1**$_c$ (%) | **10**$_c$ (%) | [**1**]$_c$ (mM) | [**1**]$_{uc}$ (mM) | [**10**]$_{uc}$ (mM) | $10^{-3}K_{a,exp}$[b] ($M^{-1}$) |
|---|---|---|---|---|---|---|---|
| 0.499 | 0.499 | 29.1 | 29.1 | 0.145 | 0.354 | 0.354 | 1.16 |
| 0.499 | 0.626 | 33.6 | 26.8 | 0.168 | 0.331 | 0.458 | 1.10 |
| 0.499 | 0.999 | 44.7 | 22.3 | 0.223 | 0.276 | 0.776 | 1.04 |
| 0.499 | 1.25 | 49.5 | 19.8 | 0.247 | 0.252 | 0.100 | 0.977 |
| 0.499 | 2.00 | 62.1 | 15.5 | 0.310 | 0.189 | 0.169 | 0.969 |
| 0.499 | 2.50 | 68.9 | 13.8 | 0.344 | 0.155 | 0.216 | 1.03 |
| 30.0 | 6.25 | 20.2 | 97.0 | 6.06 | 23.9 | 0.190 | 1.33 |
| 30.0 | 10.0 | 32.1 | 96.3 | 9.63 | 20.4 | 0.370 | 1.28 |
| 30.0 | 12.5 | 40.3 | 96.7 | 1.21 | 17.9 | 0.410 | 1.65 |
| 30.0 | 20.0 | 63.8 | 95.7 | 1.91 | 10.9 | 0.860 | 2.05 |
| 30.0 | 25.0 | 78.4 | 94.1 | 2.35 | 6.48 | 1.48 | 2.45 |

a. Subscripts "o", "c" and "uc" denote original, complexed and uncomplexed, respectively.

b. $K_{a,exp} = [\mathbf{1}]_c/\{[\mathbf{1}]_{uc}([\mathbf{10}]_0-[\mathbf{1}]_c)\}$.

**TABLE S3. Complexation of *trans*-BCMDB24C8 (2) with Dibenzylammonium Hexafluorophosphate (10) in $CD_3CN$: $CDCl_3$ (2:3) at 22±1 °C.**[a]

| $[\mathbf{2}]_0$ (mM) | $[\mathbf{10}]_0$ (mM) | $\mathbf{2}_c$ (%) | $\mathbf{10}_c$ (%) | $[\mathbf{2}]_c$ (mM) | $[\mathbf{2}]_{uc}$ (mM) | $[\mathbf{10}]_{uc}$ (mM) | $10^{-3}K_{a,exp}$[b] ($M^{-1}$) |
|---|---|---|---|---|---|---|---|
| 0.500 | 0.250 | 23.8 | 47.6 | 0.119 | 0.381 | 0.131 | 2.38 |
| 0.500 | 0.499 | 38.1 | 38.2 | 0.191 | 0.310 | 0.309 | 2.00 |
| 0.500 | 0.626 | 43.8 | 35.0 | 0.219 | 0.281 | 0.407 | 1.91 |
| 0.500 | 0.999 | 56.3 | 28.2 | 0.282 | 0.219 | 0.718 | 1.80 |
| 0.500 | 1.25 | 63.0 | 25.2 | 0.315 | 0.185 | 0.935 | 1.82 |
| 12.4 | 5.00 | 33.5 | 83.1 | 4.15 | 8.25 | 0.85 | 0.595 |
| 12.4 | 6.25 | 41.0 | 81.3 | 5.08 | 7.32 | 1.17 | 0.595 |
| 12.4 | 10.0 | 59.9 | 74.3 | 7.43 | 4.97 | 2.57 | 0.580 |
| 12.4 | 12.5 | 70.0 | 69.4 | 8.68 | 3.72 | 3.82 | 0.610 |
| 12.4 | 20.0 | 87.7 | 54.4 | 10.87 | 1.53 | 9.13 | 0.781 |

[a] Subscripts "o", "c" and "uc" denote original, complexed and uncomplexed, respectively.

[b] $K_{a,exp} = [\mathbf{2}]_c/\{[\mathbf{2}]_{uc}([\mathbf{10}]_0-[\mathbf{2}]_c)\}$.

## Analysis of Complexation Data for *cis*-Bis(carbomethoxybenzo)-24-crown-8 (1) with Dibenzylammonium Hexafluorophosphate (10) (Data for *trans*-Bis(carbomethoxybenzo)-24-crown-8 (2) with Dibenzylammonium Hexafluorophosphate (10) was analyzed analogously)

The values of apparent association constants $K_{a,exp}$ (Tables S2 and S3) show a concentration-dependence that varies two- to three-fold. This result indicates we have to take into account ion-pair dissociation effects.[S1] If H represents crown ether host **1** or **2** and $G^+X^-$ represents guest salt **10**, the three possible equilibria in solution are:

$$G^+X^- \xrightleftharpoons{K_{ipd}} G^+ + X^-$$

$$K_{ipd} = \frac{f_{\pm}^2[G^+][X^-]}{[G^+X^-]}, \quad [G^+] = \frac{K_{ipd}[G^+X^-]}{f_{\pm}^2[X^-]} \qquad (1)$$

($f_{\pm}$ = activity coefficient)

$$H + G^+ + X^- \xrightleftharpoons{K_a} H{\cdot}G^+ + X^-$$

$$K_a = \frac{[HG^+]}{[H][G^+]} = \frac{f_\pm^{\,2}[H{\cdot}G^+][X^-]}{K_{ipd}[G^+X^-][H]},$$

$$[HG^+] = \frac{K_a K_{ipd}[G^+X^-][H]}{f_\pm^{\,2}[X^-]} \qquad (2)$$

$$H + G^+X^- \xrightleftharpoons{K_{ipc}} H{\cdot}G^+X^-$$

$$K_{ipc} = \frac{[\,H{\cdot}G^+X^-]}{[H]\,[G^+X^-]},$$

$$[H{\cdot}G^+X^-] = K_{ipc}\,[H]\,[G^+X^-] \qquad (3)$$

However, formation of the ion paired complex $HG^+X^-$ along with the non-ion paired complex $H{\bullet}G^+$ would lead to concentration dependent, time averaged chemical shifts for the complex signals. This is not observed, as was previously shown for DB24C8 itself,[S1] so ion pair complexation (Eq. 3) need not be considered. The overall process is:

$$H + G^+X^- \xrightleftharpoons{K_0} H{\cdot}G^+ + X^-$$

$$K_0 = \frac{[\,H{\cdot}G^+][X^-]}{[H]\,[G^+X^-]} = \frac{K_{ipd}K_a}{f_\pm^{\,2}} = K_{a,exp}[X^-]$$

If there is no other electrolyte containing $X^-$ in the solution, $[X^-] = [G^+] + [H{\bullet}G^+]$. Substitution for $[G^+]$ and $[H{\bullet}G^+]$ from Eq. 1 and 2 yields

$$[X^-] = \left(\frac{K_{ipd}\,[G^+X^-]}{f_\pm^{\,2}}\,(1+K_a[H])\right)^{1/2} \qquad (4)$$

Then, substitution for $[X^-]$ in Eq. 2 yields

$$[H{\cdot}G^+] = \frac{K_a\,K_{ipd}\,[G^+X^-]\,[H]}{f_\pm^{\,2}\left(\dfrac{K_{ipd}\,[G^+X^-]}{f_\pm^{\,2}}(1+K_a[H])\right)^{1/2}}$$

$$= \frac{K_a\,K_{ipd}^{\,1/2}\,[G^+X^-]^{1/2}\,[H]}{f_\pm(1+K_a[H])^{1/2}} \qquad (5)$$

Eq. 5 can be simplified under two extreme conditions:

1. If $K_a[H] \gg 1$ by using high concentration of crown ether host, essentially all of the free counterion results from complexation; then

$$\frac{[\,H\cdot G^+]}{[H]^{1/2}\,[G^+X^-]^{1/2}} = \frac{K_a^{1/2}\,K_{ipd}^{1/2}}{f_\pm} \qquad (6)$$

2. If $K_a[H] << 1$ by using low concentration of crown ether host, essentially all of the free counterion results from ion pair dissociation; then

$$\frac{[\,H\cdot G^+]}{[H]\,[G^+X^-]^{1/2}} = \frac{K_a\,K_{ipd}^{1/2}}{f_\pm} \qquad (7)$$

Therefore, a plot of $[H\bullet G^+]/[G^+X^-]^{1/2}\,[H]^{1/2}$ *vs* $[G^+X^-]_0$ will yield $K_a^{1/2}\,K_{ipd}^{1/2}$ as the intercept (Eq. 6) and a plot of $[H\bullet G^+]/[G^+X^-]^{1/2}\,[H]$ *vs* $[G^+X^-]_0$ will yield $K_a\,K_{ipd}^{1/2}$ as the intercept (Eq. 7), since $f_\pm$ goes to unity as the ionic strength goes to zero and ionic strength is ultimately related to the initial concentration of the salt.

From the intercept values obtained at low concentrations ($K_a[H] << 1$) and high concentrations ($K_a[H] >> 1$) of crown ethers, $K_a$ and $K_{ipd}$ can be calculated. Using the above method (Figure S1), the $K_a$ of **1** with the dibenzylammonium cation ($C_6H_5CH_2NH_2^+CH_2C_6H_5 = G^+$) was found to be 190±67 $M^{-1}$, while $K_{ipd}$ of **10** is 6.8 (±5.5) x $10^{-3}$ M. The $K_a$ of **2** with the dibenzylammonium cation ($C_6H_5CH_2NH_2^+CH_2C_6H_5 = G^+$) was determined to be 312±35 $M^{-1}$, while $K_{ipd}$ of **10** is 4.4 (±1.2) x $10^{-3}$ M. The two independently determined values of $K_{ipd}$ for **10** agree with each other and our previous determination, considering the error.[S1] $K_{ipd}$ is independent of the host, as expected, and only related to the experimental conditions, such as solvent and temperature.

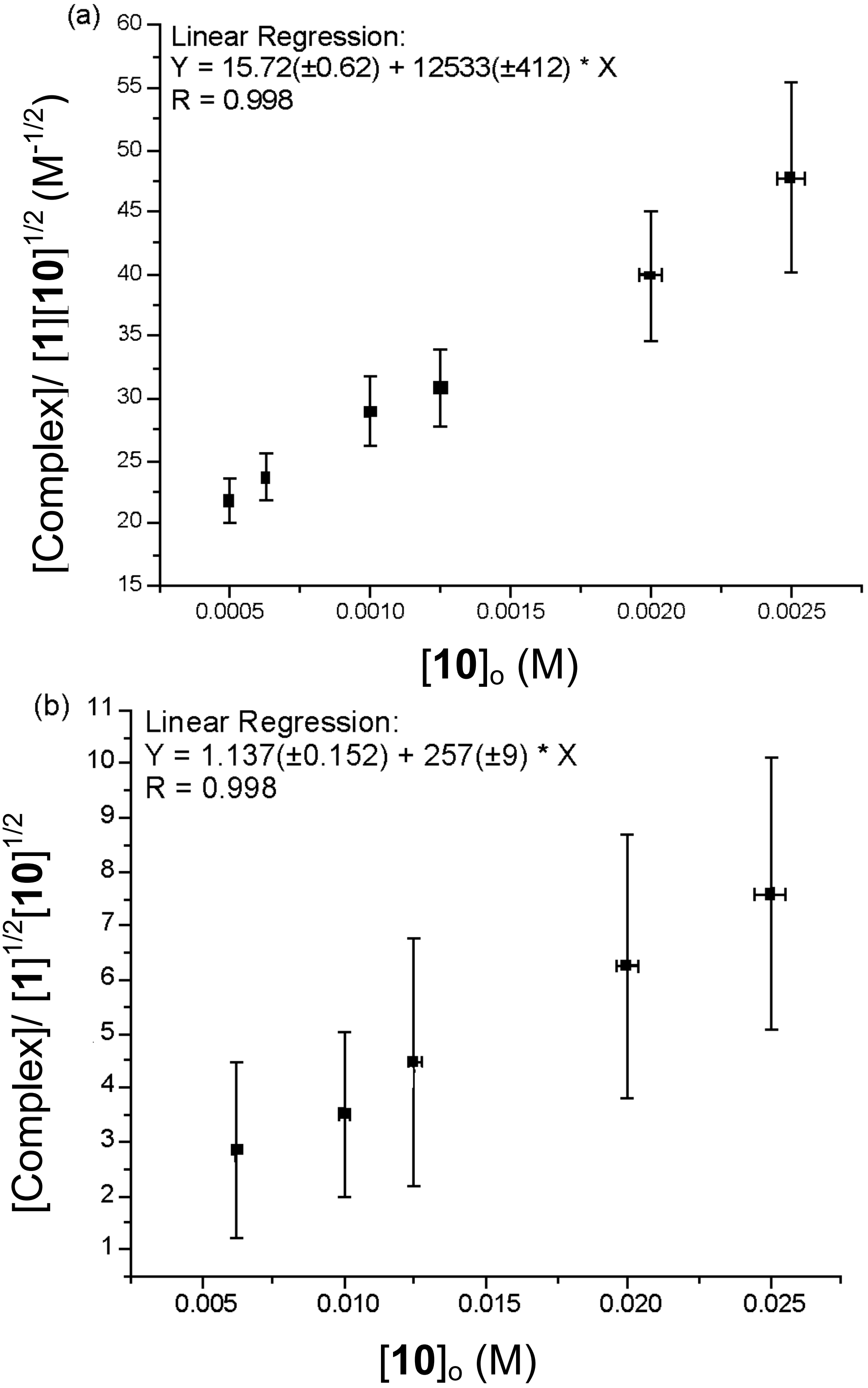


**FIGURE S1**. (a) A plot of $[\mathbf{1}]_c/[\mathbf{1}]_{uc}[\mathbf{10}]_{uc}^{1/2}$ *vs* $[\mathbf{10}]_0$ at $K_a[\mathbf{1}]_{uc} << 1$ with $[\mathbf{1}]_0 = 0.499$ mM: $K_a\ K_{ipd}^{1/2}$ = intercept = 15.7 ± 0.6 M$^{-1/2}$. (b) A plot of $[\mathbf{1}]_c/[\mathbf{1}]_{uc}^{1/2}[\mathbf{10}]_{uc}^{1/2}$ *vs* $[\mathbf{10}]_0$ at $K_a[\mathbf{1}]_{uc} >> 1$ with $[\mathbf{1}]_0 = 30.0$ mM: $K_a^{1/2}\ K_{ipd}^{1/2}$ = intercept = 1.14 ± 0.15. (Error analysis is discussed in the Experimental Section.)

## Preliminary Estimate of the Association Constant for *cis*-Bis(carbomethoxybenzo)-24-crown-8 (1) and with Potassium Hexafluorophosphate.

$^1$H NMR studies were conducted with constant concentration of **1** (0.500 mM) and varying concentrations of the salt (0.100 mM to 50.0 mM) in acetone-$d_6$. The spectra were taken at 22°C and exhibited fast exchange. Using these spectra, $\Delta_0$ was determined by extrapolation of a plot of $\Delta$ versus $1/[KPF_6]_o$ at high salt concentrations to be 0.084 ppm (Figure S2). Using this $\Delta_0$ value, since $\Delta/\Delta_o$ represents the fraction of crown ether complexed, $K_{a,exp} = (\Delta/\Delta_o)/\{1-(\Delta/\Delta_o)\}\{[KPF_6]_o-(\Delta/\Delta_o)[\mathbf{1}]_o\}$ values were determined for each solution, assuming 1:1 stoichiometry. Within this data set five points, 0.300 mM through 4.9 mM $KPF_6$, had percentage host complexed values ($\Delta/\Delta_o$) within the 20-90% range (Table S4). The 18-fold variation in $K_{a,exp}$ is consistent with the fact that the complex is not ion paired (c. f., the long F- - K distance 6.3 Å, in the crystal structure, Figure S3), but $KPF_6$ is ion paired in these solutions. Nonetheless, these results indicate

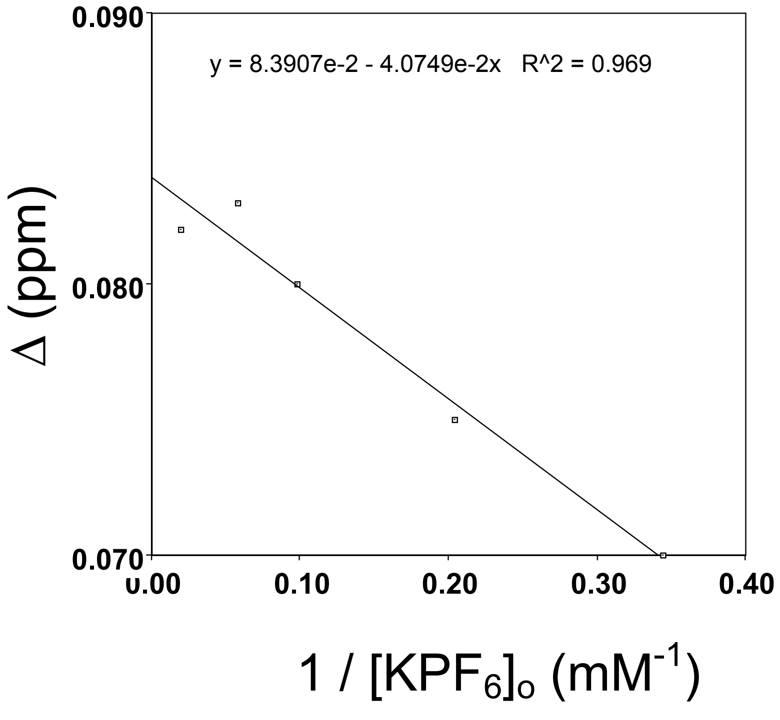


**Figure S2.** Plot of $\Delta$, the chemical shift change, of $H_\alpha/H_{\alpha'}$ of host **1** vs. the inverse of the initial concentration of $KPF_6$. The y-intercept is $\Delta_o$, the chemical shift change of $H_\alpha/H_{\alpha'}$ in the fully complexed crown ether.

rather strong complexation, as expected. More data points within the 20-80% complexation range would need to be collected to establish a reliable value of the association constant $K_a$ and the ion pair dissociation constant $K_{ipd}$ of the salt using the approach outlined above. It should be noted that the complex of 1:2 stoichiometry [(•($KPF_6$)$_2$] may also be possible, as observed with the parent DB24C8,[S2] and this may complicate the analysis.

**Table S4.** $K_{a,exp}$ Values at Different Initial Concentrations for the Complexation between **1** and $KPF_6$ in Acetone-*d*$_6$, [**1**]$_o$ = 0.500 mM

| $[KPF_6]_0$ (mM) | $\Delta^a$ (ppm) | $\Delta/\Delta_o{}^b$ | [**1**]$_c$ $^c$ (mM) | [**1**]$_{uc}$ $^d$ (mM) | $[KPF_6]_{uc}$ (mM) | $K_{a,exp,\mathbf{7\bullet4}}$ ($M^{-1}$) |
|---|---|---|---|---|---|---|
| 0.300 | 0.045 | 0.54 | 0.27 | 0.23 | 0.032 | $3.6 \times 10^4$ |
| 0.650 | 0.053 | 0.63 | 0.32 | 0.18 | 0.33 | $5.1 \times 10^3$ |
| 0.980 | 0.052 | 0.62 | 0.31 | 0.19 | 0.67 | $2.4 \times 10^3$ |
| 2.90 | 0.070 | 0.83 | 0.42 | 0.08 | 2.48 | $2.0 \times 10^3$ |
| 4.90 | 0.075 | 0.89 | 0.45 | 0.05 | 4.45 | $1.9 \times 10^3$ |

[a] For $H_\alpha/H_{\alpha'}$ of **1**.
[b] $\Delta_0$ = 0.084 ppm.
[c] "c" means complexed.
[d] "uc" means uncomplexed.

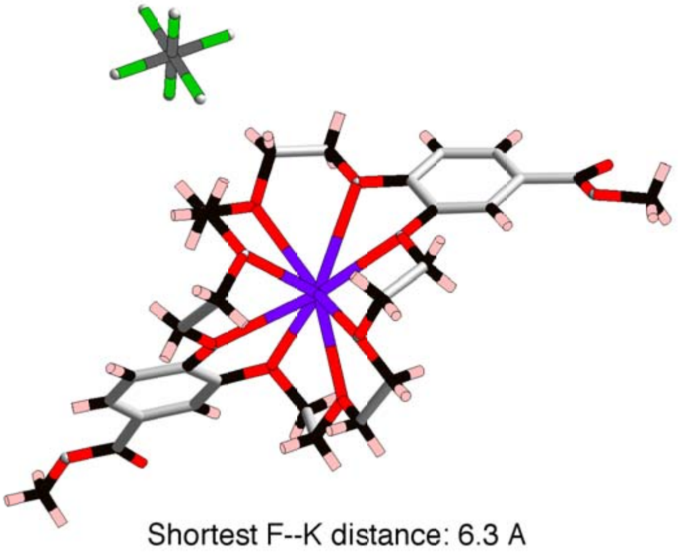


**Figure S3.** Single crystal X-ray structure of *cis*-(biscarbomethoxybenzo)-24-crown-8 (**1**) complex with $KPF_6$ showing that there is no tight ion pairing.

## Preliminary Estimate of the Association Constant for *trans*-Bis(carbomethoxybenzo)-24-crown-8 (2) and with Potassium Hexafluorophosphate.

$^1$H NMR studies were conducted with constant concentration of **2** (0.500 mM) and varying concentrations of the salt (0.0500 mM to 50.0 mM) in acetone-$d_6$. The spectra were taken at 22°C and exhibited fast exchange. Using these spectra, $\Delta_0$ was determined by extrapolation of a plot of $\Delta$ versus 1/ $[KPF_6]_o$ at high salt concentrations to be 0.142 ppm (Figure S4). Using this $\Delta_0$ value, since $\Delta/\Delta_o$ represents the fraction of crown ether complexed, $K_{a,exp} = (\Delta/\Delta_o)/\{1 - (\Delta/\Delta_o)\}\{[KPF_6]_o - (\Delta/\Delta_o)[\mathbf{2}]_o\}$ values were determined for each solution, assuming 1:1 stoichiometry. Within this data set four points, 0.400 mM through 3.1 mM $KPF_6$, had percentage host complexed values within the 20-82% range (Table S5). The 30-fold variation in $K_{a,exp}$ is consistent with the fact that the complex is not ion paired (c. f., the long F- - K distance, 6.8 Å, in the crystal structure, Figure S5), but $KPF_6$ is ion paired in these solutions. Nonetheless, these results indicate rather strong complexation, as expected. More data points within the 20-80% complexation range would need to be collected to establish a reliable value of the association constant $K_a$ and

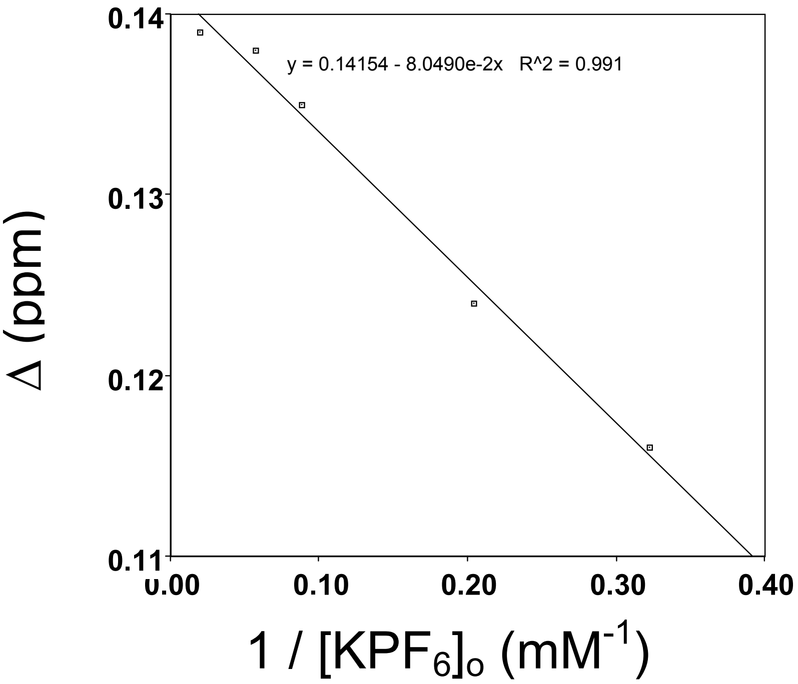


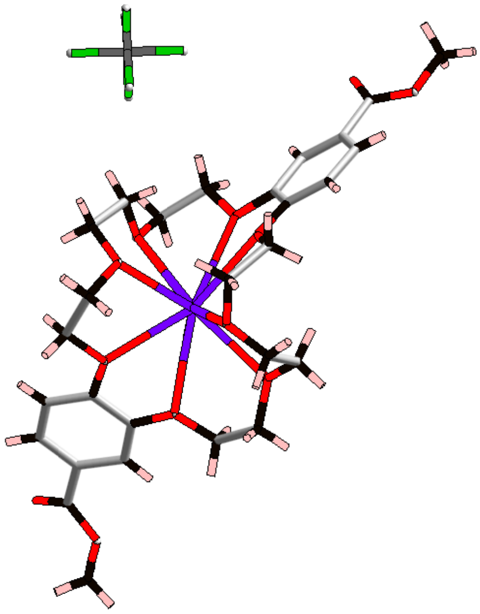
**Figure S4.** Plot of $\Delta$, the chemical shift change, of $H_\alpha/H_{\alpha'}$ of host **2** vs. the inverse of the initial concentration of $KPF_6$. The y-intercept is $\Delta_o$, the chemical shift change of $H_\alpha/H_{\alpha'}$ in the fully complexed crown ether.

the ion pair dissociation constant $K_{ipd}$ of the salt using the approach outlined above. It should be noted that the complex of 1:2 stoichiometry [(•($KPF_6$)$_2$] may also be possible, as observed with the parent DB24C8,[S2] and this may complicate the analysis.

**Table S5.** $K_{a,exp}$ Values at Different Initial Concentrations for the Complexation between **2** and $KPF_6$ in Acetone-$d_6$, [**2**]$_o$ = 0.500 mM

| $[KPF_6]_0$ (mM) | $\Delta^a$ (ppm) | $\Delta/\Delta_o{}^b$ | [**2**]$_c$ (mM) | [**2**]$_{uc}{}^d$ (mM) | $[KPF_6]_{uc}$ (mM) | $K_{a,exp,\mathbf{8 \bullet 4}}$ ($M^{-1}$) |
|---|---|---|---|---|---|---|
| 0.400 | 0.100 | 0.704 | 0.352 | 0.148 | 0.048 | $5.0 \times 10^4$ |
| 0.650 | 0.066 | 0.46 | 0.23 | 0.27 | 0.42 | $2.0 \times 10^3$ |
| 0.980 | 0.076 | 0.54 | 0.27 | 0.23 | 0.71 | $1.7 \times 10^3$ |
| 3.10 | 0.116 | 0.817 | 0.408 | 0.092 | 2.69 | $1.6 \times 10^3$ |

[a] For $H_\alpha/H_{\alpha'}$ of **2**.
[b] $\Delta_o$ = 0.142 ppm.
[c] "c" means complexed.
[d] "uc" means uncomplexed.



Shortest K--F distance: 6.8 A

**Figure S5.** Single crystal X-ray structure of *trans*-(biscarbomethoxybenzo)-24-crown-8 (**2**) complex with $KPF_6$ showing that there is no tight ion pairing.

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S1 Jones, J. W.; Gibson H. W. *J. Am. Chem. Soc.* **2003**, *125*, 7001-7004.

S2 Mercer, M.; Truter, M. R. *J. Chem. Soc., Dalton Trans.***1973**, 2469-73. Gallagher, T.; Taylor, M. J.; Ernst, S. R.; Hackert, M. L.; Poonia, N. S. *Acta Crystallogr B.* **1991**, *47*, 362-8.