

Chapter V

Selectivity Studies Among Two Hosts and Two Guests

5.1. INTRODUCTION

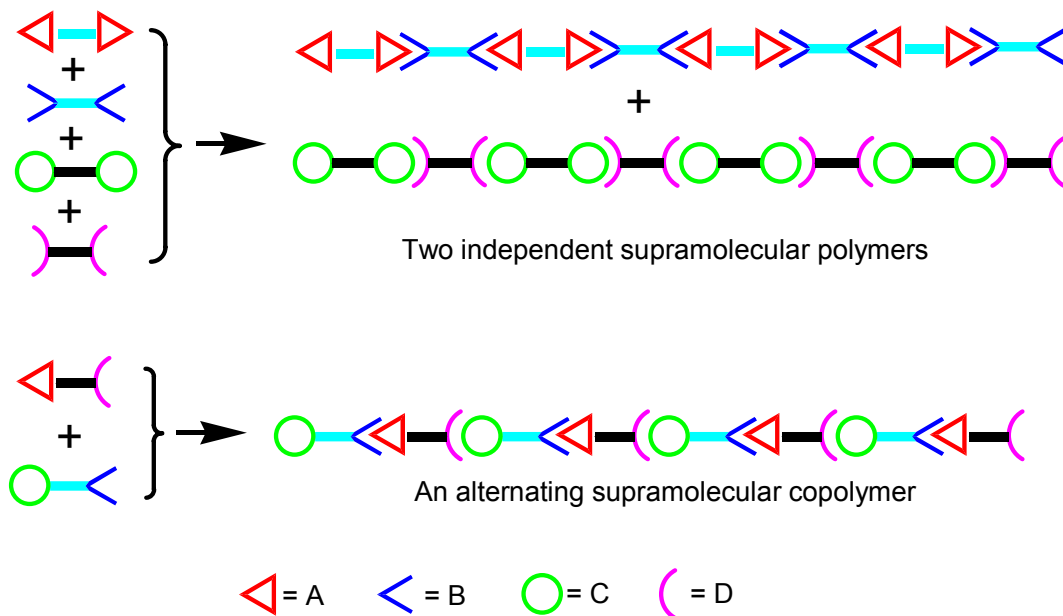
Self-assembly¹ has allowed preparation of many novel, functional, organic materials which are not easy to make by conventional synthetic tools. The construction of complicated supramolecular systems will require multiple recognition motifs in one structure.² Some examples include self-assembly of pseudorotaxanes and pseudopolyrotaxanes,^{2a} acid-base controlled molecular shuttles,^{2b} and photoinduced electron transfer triads.^{2c}

Not yet realized but intriguing in potential are selective self-assembly processes leading to formation of two distinct and independent supramolecular polymers³ from a mixture of four homoditopic building blocks, and the formation of alternating supramolecular copolymers via two molecular recognition motifs (Scheme 1). In the first case, one supramolecular polymer is based on the **A/B** recognition motif and the other one is based on the **C/D** recognition motif. The alternating supramolecular polymer is constructed from two cross-complementary heteroditopic monomer pairs **A•••D** and **C•••B**. The successful construction of such supramolecular systems requires that the complexation between **A** and **B** is much stronger than any other complexations involving

A or **B** and the complexation between **C** and **D** is much stronger than any other complexations involving **C** or **D**.

Here we report selectivity studies among two hosts, **BPP34C10** (bisparaphenylene-34-crown-10) and **DB24C8** (dibenzo-24-crown-8), and two guests, *N,N'*-dimethyl-4,4'-bipyridinium bis(hexafluorophosphate) (**1**) and dibenzylammonium hexafluorophosphate (**2**). These hosts and guests were chosen not only because they and their derivatives are most common hosts and guests in supramolecular chemistry,⁴⁻⁷ but also because we want to compare a new recognition motif, the **DB24C8**-paraquat pair,⁸ with two widely used systems: **BPP34C10**-paraquat and **DB24C8**-ammonium.⁴⁻⁶

Scheme 1. The constructions of a pair of supramolecular polymers and an alternating supramolecular copolymer via selective pairwise complexation.



When paraquat and secondary ammonium moieties were incorporated into a single ditopic guest molecule, Stoddart et al.^{2a} showed that **DB24C8** preferred to complex the ammonium group and **BPP34C10** selectively complexed the paraquat group. Further study indicated that the interaction between **DB24C8** and dibenzyl paraquat is negligible.⁹ For a long time, it has been thought that the affinity between **DB24C8** and paraquat derivatives is very weak. However, our studies here demonstrate that **DB24C8** is a better host than **BPP34C10** for **1** though **BPP34C10** has been the most used host for derivatives of **1**.^{4,6} Further we found that paraquat **1** is a better guest than ammonium salt **2** for **DB24C8**, though secondary ammonium salts have been the most used guests for **DB24C8**.^{5,6}

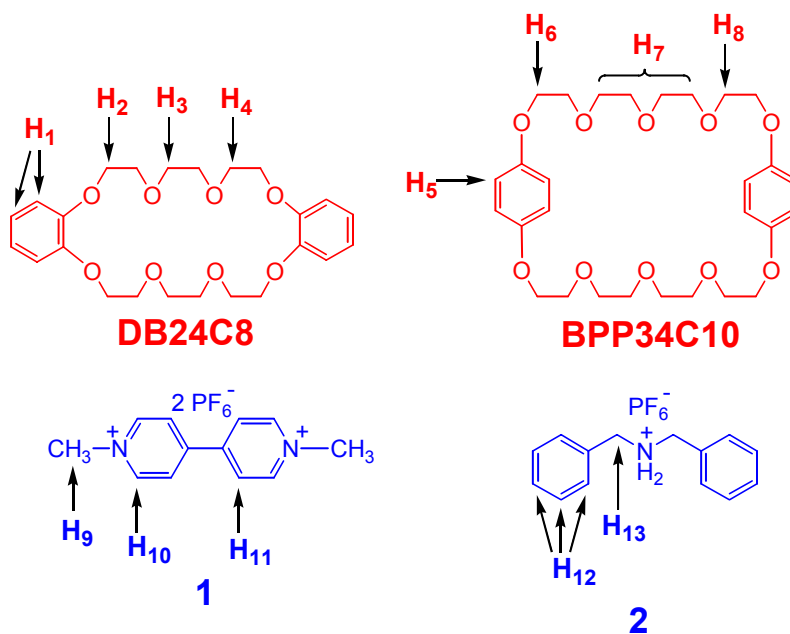


Figure 1. Compounds used in this study.

5.2. RESULTS AND DISCUSSION

A. Individual Complexation Studies.

Both the complex⁴ between **BPP34C10** and paraquat **1** and the complex⁸ between **DB24C8** and **1** are of 1:1 stoichiometry and fast exchange systems. The change of the chemical shift of H₁₁ in paraquat guest **1** upon complexation with **DB24C8** (Figures 2d, 2f) is larger than that with **BPP34C10** (Figures 2d, 2e). Benesi-Hildebrand analyses¹⁰ allowed $\Delta\delta$, the chemical shift difference between the uncomplexed and fully complexed host species, of each system to be determined (Figure 3, Figure 4, and Table 1) and correspondingly, K_a (apparent association constant) increased about three times from $6.1 (\pm 0.5) \times 10^2 \text{ M}^{-1}$ for **BPP34C10**•**1** to $1.7 (\pm 0.2) \times 10^3 \text{ M}^{-1}$ for **DB24C8**•**1** in CD₃COCD₃ (Table 1).¹¹ Therefore **DB24C8** is a better host than **BPP34C10** for **1**.

The complex^{5a} between **DB24C8** and dibenzylammonium guest **2** is of 1:1 stoichiometry and a slow exchange system (Figure 2g). From **DB24C8**•**2** to **DB24C8**•**1**, K_a increased three-fold from $5.1 (\pm 0.8) \times 10^2 \text{ M}^{-1}$ to $1.7 (\pm 0.2) \times 10^3 \text{ M}^{-1}$ (Table 1), so paraquat **1** is a better guest than the ammonium salt **2** for **DB24C8**.

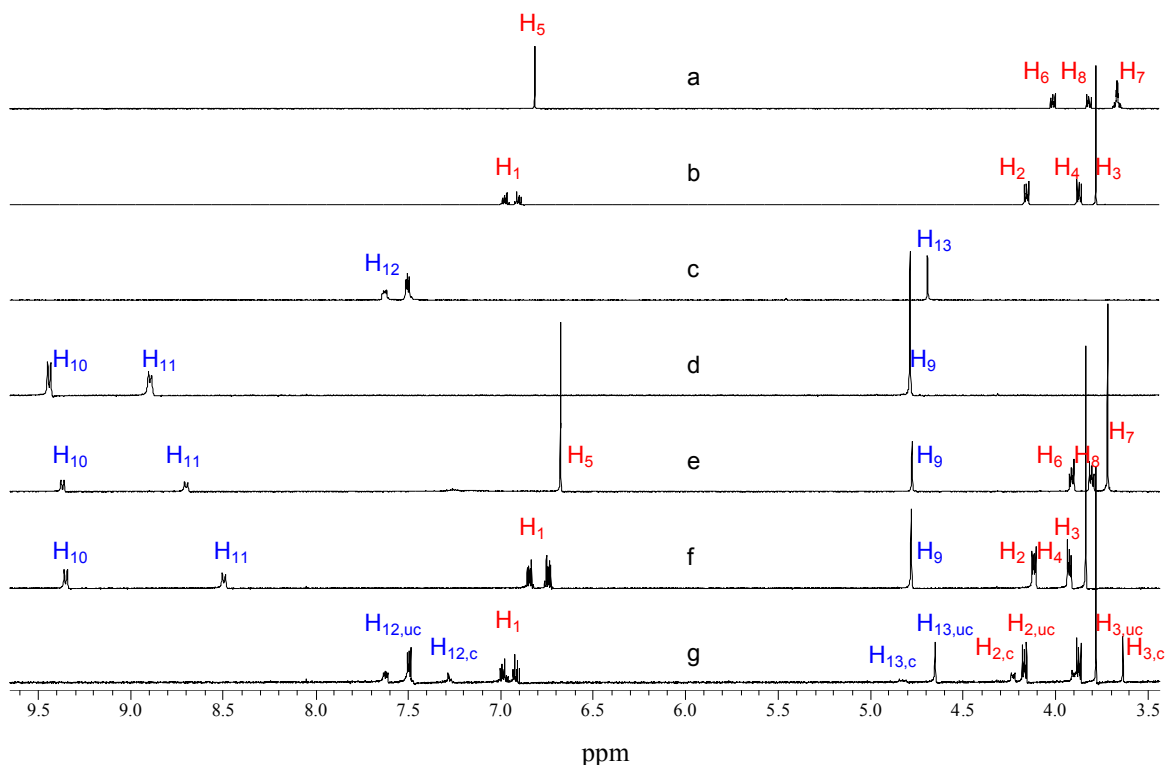


Figure 2. Partial ^1H NMR spectra (400 MHz, CD_3COCD_3 , 298K) of (a) 1.00 mM **BPP34C10**, (b) 1.00 mM **DB24C8**, (c) 1.00 mM **2**, (d) 1.00 mM **1**, (e) 1.00 mM **BPP34C10** and 1.00 mM **1**, (f) 1.00 mM **DB24C8** and 1.00 mM **1**, and (g) 1.00 mM **DB24C8** and 1.00 mM **2**.

Table 1. Complexes of Host Crown Ethers with Guest Salts.

Complexes	Stoichiometry H:G	Exchange	Probe Hydrogen	Δ_0 (ppm)	K_a (M^{-1}) ^b
BPP34C10•1	1:1 ⁴	Fast	H ₅	0.467	$6.1 (\pm 0.5) \times 10^2$
DB24C8•1	1:1 ⁸	Fast	H ₃	0.120 ^a	$1.7 (\pm 0.2) \times 10^3$
DB24C8•2	1:1 ^{5a}	Slow	H ₃	—	$5.1 (\pm 0.8) \times 10^2$

^a Determined in Chapter 2.

^b At 1.00 mM initial concentrations of host and guest in CD₃COCD₃.^{11,13}

B. Competitive Complexation of Hosts DB24C8 and BPP34C10 with Paraquat Guest 1.

The proton NMR spectrum of a solution of 1.00 mM **BPP34C10**, 1.00 mM **DB24C8**, and 1.00 mM **1** is shown in Figure 3d. By comparing the chemical shift of H₅ in this spectrum with that of H₅ under uncomplexed status (Figure 3a), the difference is 0.109 ppm. Δ_0 of H₅ is 0.467 ppm (Table 1), so the concentration of complexed **BPP34C10** can be estimated to be 0.23 mM. Correspondingly, from the change of chemical shift of H₃ in **DB24C8**, the concentration of complexed **DB24C8** is estimated to be 0.38 mM. Therefore, about twice as much **1** complexed with **DB24C8** than with **BPP34C10**; that is, **DB24C8** is a better host than **BPP34C10** for **1**. This result agrees with the individual complexation studies. Apparent association constants calculated for **BPP34C10•1** and **DB24C8•1** in this solution were $7.7 (\pm 1.2) \times 10^2 M^{-1}$ and $1.6 (\pm 1.4) \times 10^3 M^{-1}$ (Errors were calculated based on errors in complexed concentrations of **DB24C8**, **BPP34C10**, and **1**). They are very close to the values obtained in the individual

complexation studies (Table 1). Therefore, the two complexations did not detectably affect each other.

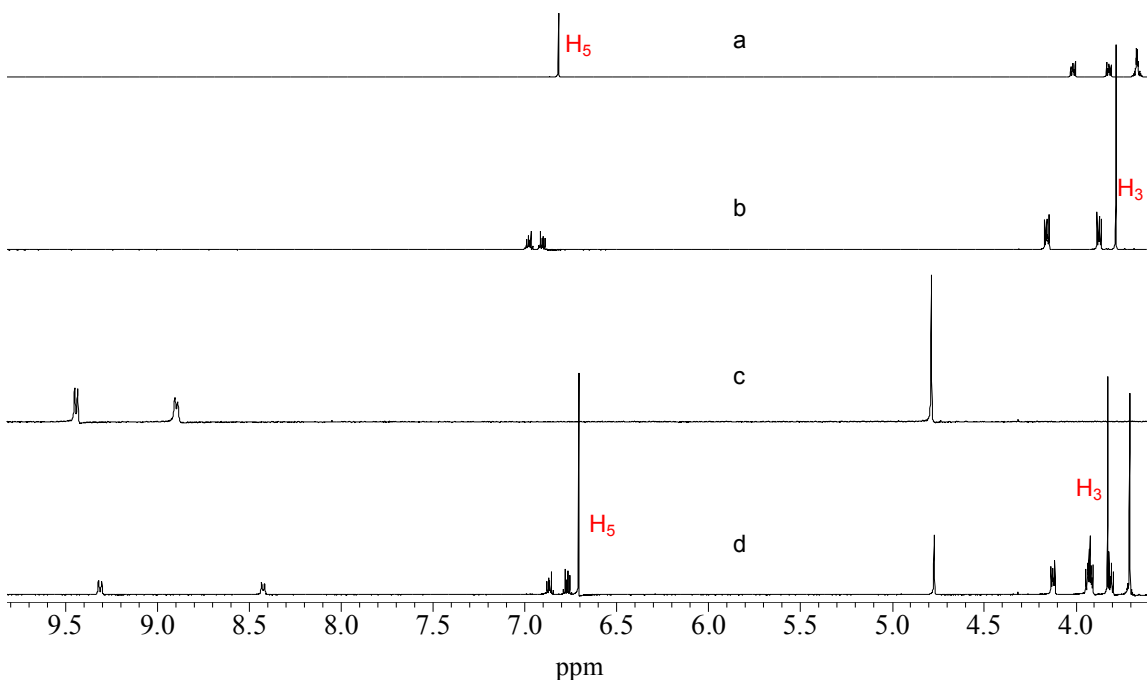


Figure 3. Partial ^1H NMR spectra (400 MHz, CD_3COCD_3 , 298K) of (a) 1.00 mM **BPP34C10**, (b) 1.00 mM **DB24C8** (c) 1.00 mM **1**, (d) 1.00 mM **BPP34C10**, 1.00 mM **DB24C8**, and 1.00 mM **1**.

C. Competitive Complexation of Guests **1** and **2** with Host **DB24C8**.

The proton NMR spectrum of a mixture of 1.00 mM **DB24C8**, 1.00 mM **1**, and 1.00 mM **2** is shown in Figure 4d. From the change of chemical shift of H_{11} in **1**, the concentration of complexed **1** is calculated to be 0.26 mM.¹⁴ From integrations of peaks corresponding to complexed ($\text{H}_{12,\text{c}}$) and uncomplexed ($\text{H}_{12,\text{uc}}$) aromatic hydrogen atoms in **2**, the concentration of complexed **2** is determined to be 0.12 mM. Therefore, ca. twice

as much **DB24C8** complexes with **1** than with **2**; that is, paraquat **1** is a better guest than ammonium salt **2** for host **DB24C8**. K_a calculated for the complexes **DB24C8•1** and **DB24C8•2** in this study were $5.7 (\pm 1.0) \times 10^2 \text{ M}^{-1}$ and $2.2 (\pm 0.5) \times 10^2 \text{ M}^{-1}$ (Errors were calculated based on errors in complexed concentrations of **DB24C8**, **1** and **2**). These values are lower than the values obtained in the individual complexation studies (Table 1). The reason for this decrease is the common ion effect, i. e., the increase in free counterion concentration due to the two complexation processes, on ion pairing equilibria.¹²

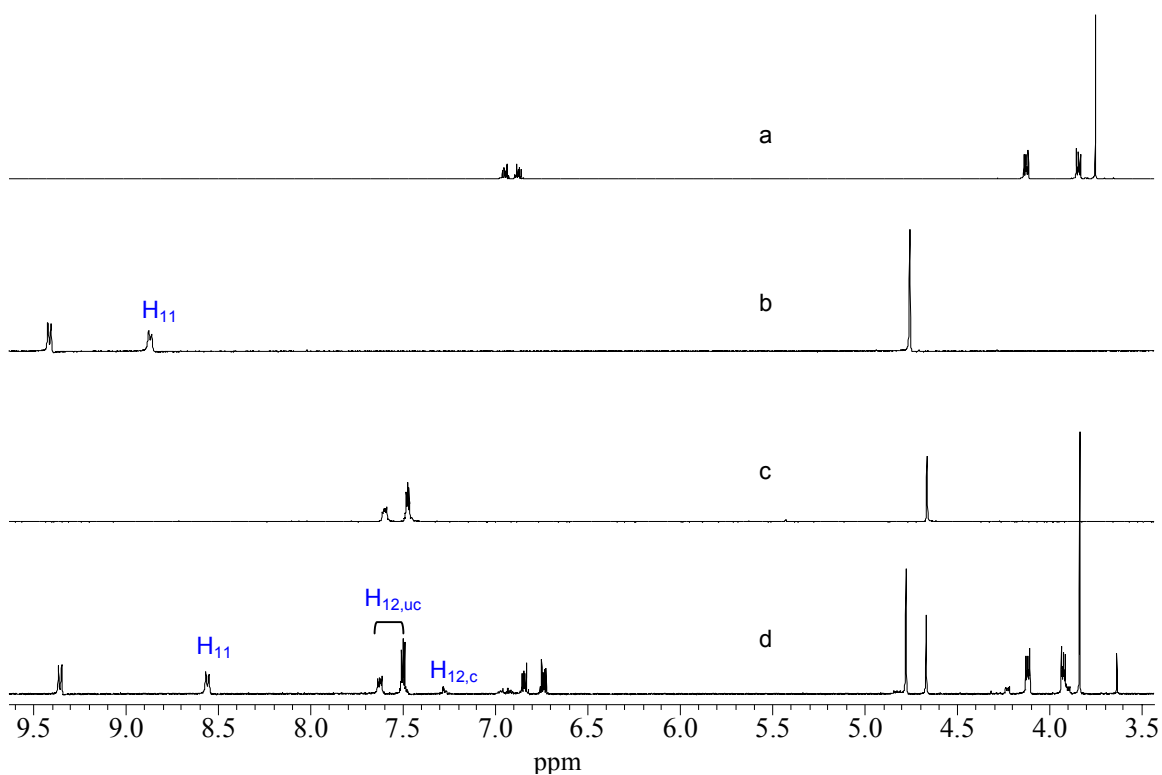


Figure 4. Partial ^1H NMR spectra (400 MHz, CD_3COCD_3 , 298K) of (a) 1.00 mM **DB24C8**, (b) 1.00 mM **1** (c) 1.00 mM **2**, (d) 1.00 mM **DB24C8**, 1.00 mM **1**, and 1.00 mM **2**.

5.3. CONCLUSIONS

In summary, by individual and competitive complexation studies, we have demonstrated that **DB24C8** is a better host than **BPP34C10** for paraquat **1**, and that paraquat **1** is a better guest than the ammonium salt **2** for host **DB24C8**. These selectivity studies provide useful information; they demonstrate that these molecular recognition motifs' selectivities are not sufficient to make supramolecular polymers of the types shown in Scheme 1 in a well-controlled manner. More selective and more efficient pairs are being pursued.¹⁵

5.4. ACKNOWLEDGEMENTS

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5.5. EXPERIMENTAL

DB24C8 was purchased and used as received. All other compounds were prepared by literature procedures.

The 400 MHz ¹H NMR spectra were recorded on a Varian Inova Instrument.

For the 1:1 complex between **DB24C8** and **2**,^{5a} a slow exchange system, the uncomplexed and complexed host or guest concentrations and apparent association constants (K_a) were calculated based on integration of proton NMR spectra. For the 1:1 complex between **BPP34C10** and **1**^{4a} and the 1:1 complex between **DB24C8** and **1**, two fast exchange systems, ¹H NMR characterizations were done on solutions with constant

[host]₀ (**BPP34C10** or **DB24C8**) and [guest]₀ (**1**) was varied from one to fifty times [host]₀. Based on these NMR data, $\Delta\theta$, the difference in δ values for protons of the host or guest in the uncomplexed and fully complexed species, was calculated by using the Benesi-Hildebrand method.¹⁰ The complexed host and guest concentrations are represented by [host]_c or [guest]_c, while [host]_{uc} and [guest]_{uc} represent the uncomplexed host and guest concentrations. Then [host]_c = [guest]_c = $(\Delta/\Delta\theta)[\text{host}]_0$, [host]_{uc} = $(1 - \Delta/\Delta\theta)[\text{host}]_0$, [guest]_{uc} = [guest]₀ - [guest]_c, $K_a = [\text{host}]_c / \{[\text{host}]_{uc} [\text{guest}]_{uc}\}$.

All solutions were prepared as follows. Precisely weighed amounts of dried chemicals were added into screw cap vials. Acetone-*d*₆ was added with to-deliver volumetric pipets. Then specific volumes of each fresh solution were mixed to yield the desired concentrations. For example, in order to make a solution, 1.00 mM **1**, 1.00 mM **DB24C8** and 1.00 mM **BPP34C10**, three solutions, 2.00 mM mM solution of **1**, 2.00 mM mM solution of **DB24C8**, and 2.00 mM mM solution of **BPP34C10**, were made first by adding 5.00 mL acetone-*d*₆ with a 5.00 mL to-deliver pipette into three screw cap vials containing 7.04 mg (0.0150 mmol) of **1**, 6.72 mg (0.0150 mmol) of **DB24C8**, 8.04 mg (0.0150 mmol) of **BPP34C10** separately. Then 0.300 mL of each solution was added with a 0.300 mL to-deliver pipet into a vial. ¹H NMR data were collected on a temperature controlled spectrometer. Acetone-*d*₆ was chosen as the solvent because all compounds used here have good solubilities in it. Error bars were calculated by assuming a $\pm 5\%$ deviation in percent complexation ($\Delta/\Delta\theta$). Linear regressions were performed using the entire error range (abscissa and ordinate) at each data point; standard errors in both the intercept and slope coefficients based on regression were used to determine errors in association constants.

Keywords: bisparaphenylene-34-crown-10, dibenzo-24-crown-8, paraquat, ammonium salt, pseudorotaxane complex

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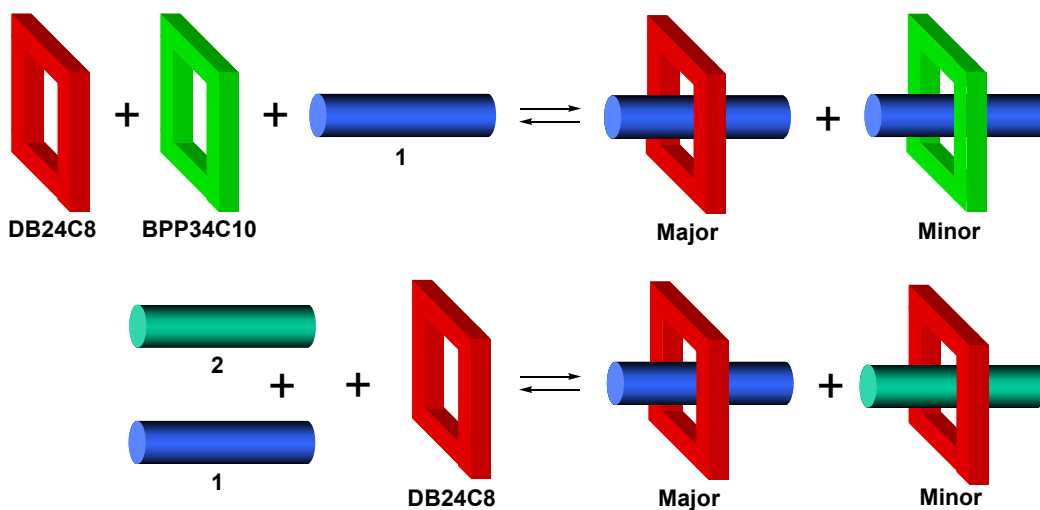
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 11. For example, the apparent association constant of **DB24C8•1** was calculated in this way. ¹H NMR characterization was done on solutions with constant **[DB24C8]₀** and varied **[1]₀**. Based on the NMR data, Δ_0 , the difference in δ values for H₃ of **DB24C8** in the uncomplexed and fully complexed species, was calculated by using the Benesi-Hildebrand method.¹⁰ Then K_a was calculated from $K_a = (\Delta / \Delta_0)[\mathbf{DB24C8}]_0 / \{ \{ [\mathbf{DB24C8}]_0 - (\Delta / \Delta_0)[\mathbf{DB24C8}]_0 \} \{ [\mathbf{1}]_0 - (\Delta / \Delta_0)[\mathbf{DB24C8}]_0 \} \}$. Errors were calculated by assuming $\pm 5\%$ error in Δ / Δ_0 . We found that apparent association constants K_a for these systems are concentration dependent,¹² so it is necessary to specify initial concentrations.
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 13. Errors were calculated by assuming $\pm 5\%$ error in integrations. We found that the apparent association constant K_a of **DB24C8•2** is concentration dependent, so it

is necessary to specify initial concentrations.¹²

14. $\Delta\theta$ of H₁₁ in the complexation between **DB24C8** and **1** is 1.303 ppm calculated by using the Benesi-Hildebrand method.¹⁰
15. This type of host-guest complexation differs from the selective dimerization or aggregation of individual molecules (“self-sorting”) as recently discussed in Wu, A.; Issacs, L. *J. Am. Chem. Soc.* **2003**, *125*, 4831-4835.

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Abstract: As shown by self-selectivity studies among two hosts, **BPP34C10** (bisparaphenylene-34-crown-10) and **DB24C8** (dibenzo-24-crown-8), and two guests, N,N'-dimethyl-4,4'-biyridinium bis(hexafluorophosphate) (**1**) and dibenzylammonium hexafluorophosphate (**2**), **DB24C8** is a better host than **BPP34C10** for **1** and **1** is a better guest than **2** for **DB24C8**.
