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Complexation of 1,4-Bis(pyridinium)butanes by Negatively Charged Carboxylatopillar[5]arene

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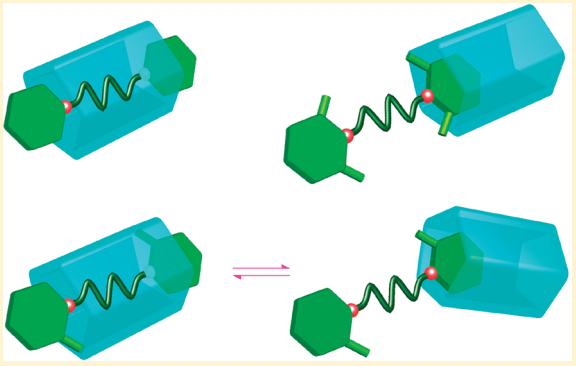
Supporting Information

ABSTRACT: The binding behavior of substituted 1,4-bis(pyridinium)butane derivatives (X-Py$(CH_2)_4$Py-X, X = H, 2-methyl, 3-methyl, 4-methyl, 2,6-dimethyl, 4-pyridyl, and 4-COOEthyl) $\mathbf{1}^{2+}$−$\mathbf{7}^{2+}$, with negatively charged carboxylatopillar[5]arene (CP5A) has been comprehensively investigated by ^{1}H NMR and 2D ROESY and UV absorption and fluorescence spectroscopy in aqueous phosphate buffer solution (pH 7.2). The results indicated that the position of the substituents attached on pyridinium ring dramatically affects the association constants and binding modes. 3- and 4-Substituted guests ($\mathbf{1}^{2+}$, $\mathbf{3}^{2+}$, $\mathbf{4}^{2+}$, $\mathbf{6}^{2+}$, $\mathbf{7}^{2+}$) form [2]pseudorotaxane geometries with CP5A host, giving very large association constants (>10^5 M^{-1}), while 2,6-dimethyl-substituted $\mathbf{5}^{2+}$ forms external complex with relatively small K_a values [$(2.4 \pm 0.3) \times 10^3$ M^{-1}] because the 2,6-dimethylpyridinium unit is too bulky to thread the host cavity. Both of the binding geometries mentioned above are observed for $\mathbf{2}^{2+}$, having one methyl group in the 2-position of pyridinium. Typically, the association constant of [2]pseudorotaxane $\mathbf{1}^{2+}\subset$CP5A exceeds 10^6 M^{-1} in water, which is significantly higher than those of previously reported analogues in organic solvents. The remarkably improved complexation of bis(pyridinium) guests by the anionic host was due to electrostatic attraction forces and hydrophobic interactions.

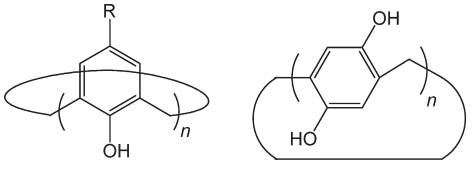


INTRODUCTION

Threaded structures, such as rotaxanes and catenanes, are the focus of increasing research interest not only for their topological importance but also due to their inventive applications.[1] Pseudorotaxanes[2] are the supramolecular precursors of rotaxanes and catenanes. The macrocyclic hosts, such as crown ethers,[3−6] cyclodextrins,[7,8] and cucurbiturils,[8−10] have been widely used in construction of pseudorotaxane structures as wheel components. Calixarenes, on the other hand, are somewhat difficult to convert to pseudorotaxane-type complexes[11,12] due to their "basket" structures, despite their tunable size, facile modification, and special binding characteristics.[13−16]

Pillar[n]arene (PnA, n = 5, 6) is a new calixarene analogue made up of hydroquinone units linked by methylene (−CH_2−) bridges. (Scheme 1) Being different from the conventional calixarene's "basket" structure, PnA forms the symmetrical pillar architecture, and its two cavity portals are identical. The structural features of PnA make it superior to calixarene in the construction of pseudorotaxanes and rotaxanes.[17−19] Our previous work[17a] has reported the formation of a series of 1:1 [2]pseudorotaxanes and 2:1 host−guest complexes between P5A with dicationic 1,4-bis(pyridinium)butanes and alkyl-substituted paraquat derivatives. Recently, we[17b] also reported the first PnA-based [2]pseudorotaxane molecular switch formed by a bis(imidazolium) dication and P5A host, in which the dethreading/rethreading process can be easily controlled by base−acid stimuli. Charge−transfer interactions between host and pyridinium or imidazolium cations are certainly the major driving forces during the complexation. However, for the two host−guest systems K_a values are too low (less than 10^3 M^{-1}). In order to prepare interlocked molecules and large supramolecular architectures efficiently, it is necessary to increase the association strength between P5A with linear axle components. Building on

Scheme 1. Structures of Calixarenes and Pillararenes



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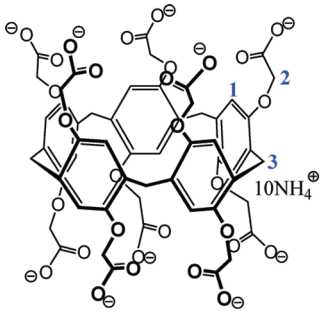
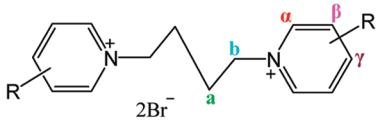
Scheme 2. Structure and Proton Designations of the Host and the Guests



CP5A



$\mathbf{1}^{2+}$	R = H	$\mathbf{5}^{2+}$	R = 2,6-diCH$_3$
$\mathbf{2}^{2+}$	R = 2-CH$_3$	$\mathbf{6}^{2+}$	R = 4-(4-Pyridyl)
$\mathbf{3}^{2+}$	R = 3-CH$_3$	$\mathbf{7}^{2+}$	R = 4-COOCH$_2$CH$_3$
$\mathbf{4}^{2+}$	R = 4-CH$_3$		

our previous studies, we asked ourselves whether and to what extent the introduction of electrostatic attraction, one of the strongest noncovalent interactions possible, would improve the host−guest complexation. Thus, we chose a series of cationic 1,4-bis(pyridinium)butane guests (with bromide counteranions) depicted in Scheme 2 and screened their interactions with a negatively charged P5A, carboxylatopillar[5]arene (CP5A, Scheme 2). ^{1}H NMR, 2D ROESY, UV, and fluorescence results provide converging evidence of the highly effective binding and [2]pseudorotaxane formation in neutral aqueous solution.

RESULTS AND DISCUSSION

^{1}H NMR Results. Figure 1 shows the ^{1}H NMR spectra of $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, and $\mathbf{5}^{2+}$ in D_2O recorded in the absence and in the presence of approximately 1.0 equiv of host. As can be seen from Figure 1b, in the presence of about 1 equiv of CP5A, proton signals of $\mathbf{1}^{2+}$ derived from methylene (H_a and H_b) of the linked chain and α pyridinium aromatic proton (H_α) exhibit very pronounced upfield displacement ($\Delta\delta$ = −2.38, −2.26, and −1.17 ppm for H_a, H_b and H_α, respectively), while no obvious changes were observed for the β- and γ- protons. The host-induced upfield shifts on the pyridine α-protons and methylene protons reveal that the host engulfs the central part, which thus leads to an efficient shield[20] toward guest protons. Similar CP5A complexation-induced effects are observed for guests $\mathbf{3}^{2+}$, $\mathbf{4}^{2+}$, $\mathbf{6}^{2+}$, and $\mathbf{7}^{2+}$, possessing 3-methyl, 4-methyl, 4-pyridyl, and 4-COOEt substituents. Because of the similar complexation effects observed with these five axles mentioned above, the guests must have a similar mode of binding with CP5A. That is to say, the CP5A wheel is fully threaded by the axles and the main binding site for the host is the methylene linker. Meanwhile, part of the pyridinium ring (N^+ and α-position) is also included in the host cavity. These inclusion complexes can be considered to have [2]pseudorotaxane structures.

In contrast, when two methyl groups are substituted to the 2- and 6- position of the pyridinium ring, affording $\mathbf{5}^{2+}$, very different signal changes are observed from NMR spectra (Figure 1d). In the presence of CP5A, no obvious signal changes are observed for the proton signals of the methylene linker (H_a and H_b), indicating that the pseudorotaxane-type complex does not form. This is reasonable because the 2,6-dimethylpyridinium unit is too bulky to thread through the cavity of host. Meanwhile, the β- and γ-pyridinium aromatic protons exhibit significant upfield displacement (−0.39 and −0.46 for H_β and H_γ), indicating that the binding site for $\mathbf{5}^{2+}$ is located at the pyridinium ring.

For $\mathbf{2}^{2+}$, having one methyl group in the α-position of the pyridinium ring, the CP5A-induced changes in the ^{1}H NMR spectrum clearly depart from those observed with $\mathbf{1}^{2+}$ and $\mathbf{5}^{2+}$. Figure 1f shows the corresponding spectra. Notice that a new species occurs, indicating slow exchange on the NMR time scale. The resonances of the new species are consistent with the formation of an interpenetrated complex, and the peaks for the methylene protons (Figure 1f) exhibit substantial upfield shifts ($\Delta\delta \approx -2.10$ and −2.00 ppm for H_a' and H_b') as a consequence of inclusion-induced shielding effects.[20] The signals for the β- and γ-protons (Figure 1f, $H_{\beta1'}$, $H_{\beta2'}$, and $H_{\gamma'}$) shift downfield no more than 0.30 ppm, while those for the α-protons (Figure 1f, $H_{\alpha'}$) exhibit upfield shifts of 1.12 ppm. This set of NMR species shows the internal complexation between $\mathbf{2}^{2+}$ and CP5A (similar with guest $\mathbf{1}^{2+}$, $\mathbf{3}^{2+}$, $\mathbf{4}^{2+}$, $\mathbf{6}^{2+}$, and $\mathbf{7}^{2+}$). However, different from the general slow exchange process,[5,17a,21] no uncomplexed signals were observed. Another set of NMR species represents the formation of external complex (similar with $\mathbf{5}^{2+}$), since the peaks for pyridinium protons exhibit upfield shifts (Figure 1f, $\Delta\delta$ = −0.39, −1.00, −0.67, and −0.96 ppm for $H_{\alpha'}$, $H_{\beta1'}$, $H_{\beta2'}$, and $H_{\gamma'}$, respectively) and those for methylene protons (Figure 1f, H_a and H_b) do not shift. These NMR changes indicate that $\mathbf{2}^{2+}$ forms either a pseudorotaxane-type inclusion complex at the methylene linker (slow exchange kinetics) or an external complex at the pyridinium ring (fast exchange kinetics). On the other hand, the $\Delta\delta$ values for the $\mathbf{2}^{2+}$/CP5A external complex show a unique order of γ-H/β1-H > α-H/β2-H. A possible reason may be that the 2-methylpyridinium group of $\mathbf{2}^{2+}$ is included in the CP5A cavity in an acclivitous orientation, which is different from the perpendicular manner of $\mathbf{5}^{2+}$ (see Figure 4).

Two-Dimensional NMR Experiments. To further confirm the different binding modes, the ROESY spectra of $\mathbf{1}^{2+}\subset$ CP5A and $\mathbf{5}^{2+}\subset$CP5A complexes were measured in D_2O. As shown in Figure 2, the 2D NMR examinations of a mixture of $\mathbf{1}^{2+}$ (3.1 mM) and CP5A (3.6 mM) exhibited unequivocal correlation peaks between methylene protons (H_a/H_b) of $\mathbf{1}^{2+}$ and the host's aromatic protons (H_1); see the NOE cross-peaks A and B, respectively. In the aromatic region of guest, there are clear correlations between pyridinium α-protons of $\mathbf{1}^{2+}$ (H_α) and the host's H_1 protons, which are denoted as C. However, no appreciable cross-peak between the pyridinium β/γ-protons and H_1 were observed. On the other hand, there are correlations between $H_a/H_b/H_\alpha/H_\beta$ protons of $\mathbf{1}^{2+}$ and CP5A's H_2 protons, which are denoted as D, E, F, and G, respectively, while no cross-peaks between the pyridinium γ-protons and H_2 were observed. These observations indicate

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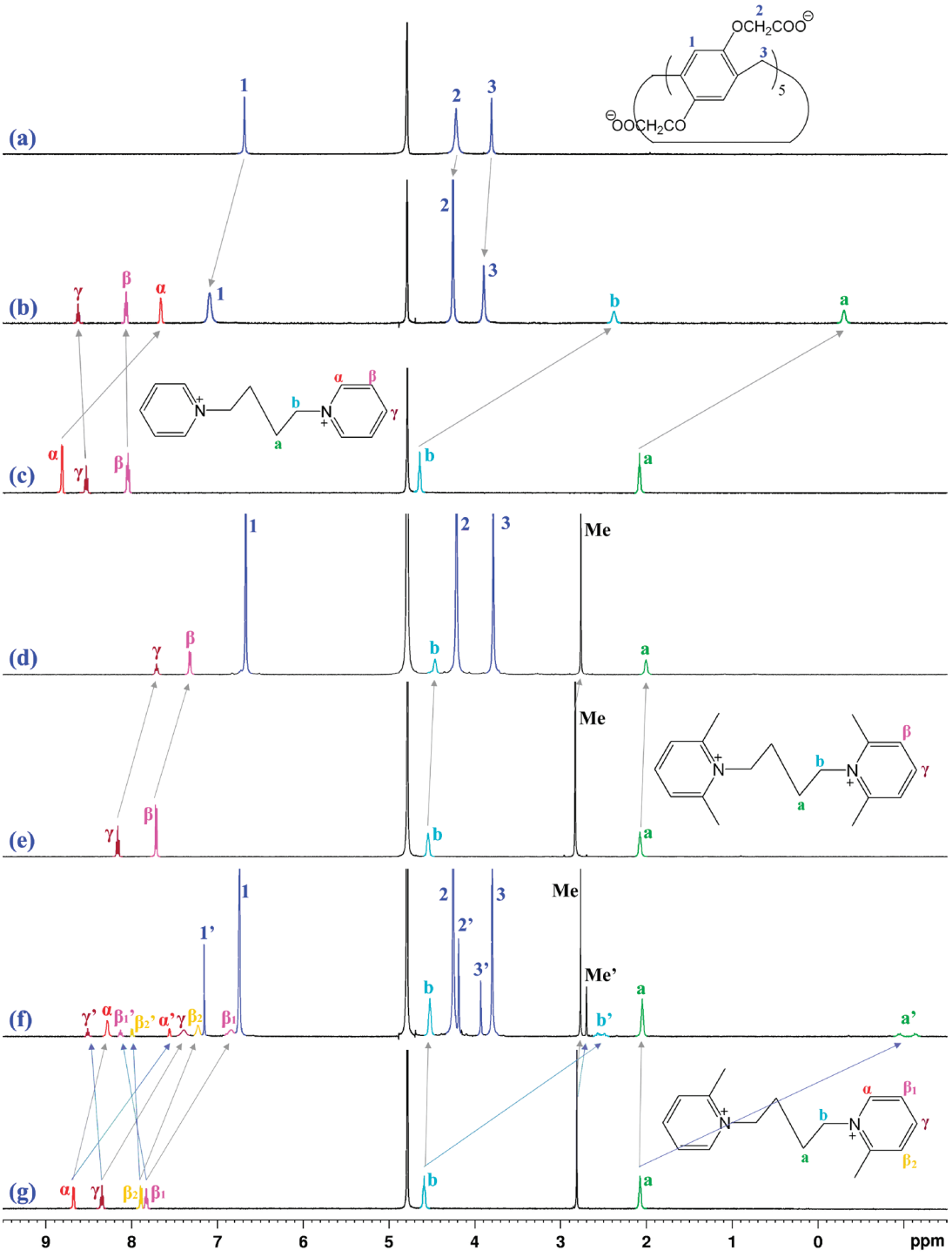

Figure 1. ^{1}H NMR spectra (500 MHz) of (a) CP5A, (b) $\mathbf{1}^{2+}$, (c) CP5A + $\mathbf{1}^{2+}$, (d) CP5A + $\mathbf{5}^{2+}$, (e) $\mathbf{5}^{2+}$, (f) CP5A + $\mathbf{2}^{2+}$, and (g) $\mathbf{2}^{2+}$ in D_2O at 3.0−3.7 mM.

that $\mathbf{1}^{2+}$ is fully included into the CP5A cavity to form the [2]pseudorotaxane-type complex.

In sharp contrast to $\mathbf{1}^{2+}\subset$CP5A, the $\mathbf{5}^{2+}\subset$CP5A complex does not show NOE correlations between the methylene residues (H_a/H_b) and the host's H_1 protons (Figure 3), indicating that the CP5A bead does not reach the central methylene nucleus of the guest. On the other hand, there are clear correlations between β-protons of pyridinium H_β with H_1 (see the NOE cross-peaks A). Thus, the main binding site of $\mathbf{5}^{2+}\subset$CP5A is the pyridium residues of the guest.

Combining these 2D ROESY results with ^{1}H NMR spectral studies mentioned above, we can definitely conclude the different binding modes induced by the substituents of 1,4-bis(pyridinium)-butane. Meta- and para-position substituted groups do not change the [2]pseudorotaxane-type modes. In contrast, when the two ortho-positions of pyridinium were substituted by methyl groups, affording $\mathbf{5}^{2+}$, the external complex at pyridinium ring was formed. Both of the binding modes are observed for $\mathbf{2}^{2+}$, having one methyl group in the ortho-position of pyridinium (Figure 4).

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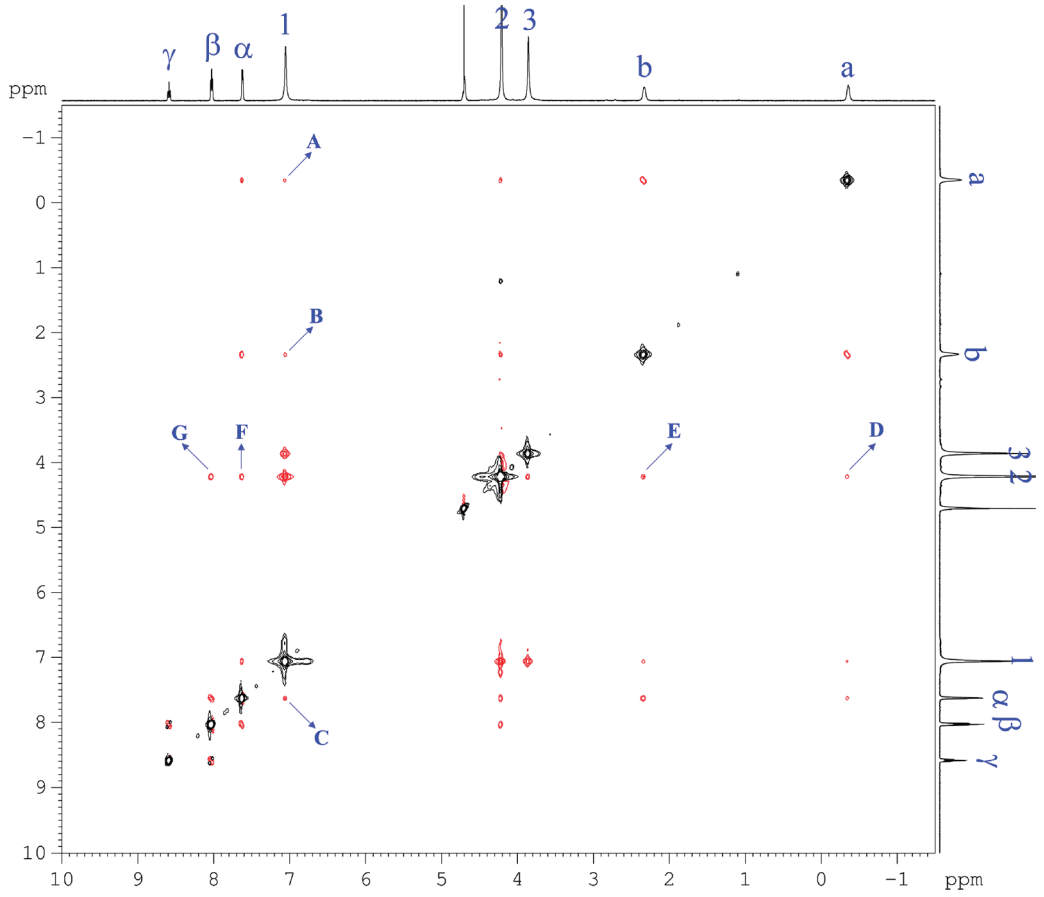

Figure 2. 2D ROESY analysis of $\mathbf{1}^{2+}$ with CP5A in D_2O with a mixing time of 200 ms (500 MHz, 298.15 K; the concentrations of host and guest are 3.6 and 3.1 mM, respectively).

Charge Transfer. As can be seen from Figure 5, upon addition of bis(pyridinium) axles to the aqueous solution of CP5A, different spectroscopic behaviors were observed. The equimolar mixture of CP5A and $\mathbf{1}^{2+}$ shows a relatively weak CT absorption. The substitution of electron-donating methyl groups ($\mathbf{2}^{2+} \sim \mathbf{5}^{2+}$) to $\mathbf{1}^{2+}$ does not change the CT band obviously, while the introduction of pyridyl groups ($\mathbf{6}^{2+}$) and COOEt groups ($\mathbf{7}^{2+}$) significantly improves the CT absorption (~380 nm), leading the complex to become light yellow and yellow, respectively. Pyridyl and COOEt are stronger electron-withdrawing groups, and the resulting increased charge−transfer interaction leads to the stronger CT effect. Therefore, the chromophoric sensor behavior of complexation between CP5A and bis(pyridinium) cations in water can be controlled by changing the substituting groups of the axles. This complexation-induced CT absorption for CP5A is similar to that observed in the P5A−1,4-bis(pyridinium)-butane and dibenzo-24-crown-8−1,2-bis(pyridinium)ethane inclusion complex, as previously reported by us.[17a,21]

Molecular Binding Ability and Molecular Recognition. To quantitatively assess the inclusion complexation behavior of these compounds, fluorescence titrations of CP5A with guests $\mathbf{1}^{2+}$−$\mathbf{7}^{2+}$ were performed at 298.15 K in a phosphate buffer solution of pH 7.2 (Figure 6). Assuming 1:1 inclusion complexation stoichiometry between CP5A and the seven guests, the association constants (K_a) could be calculated by using a nonlinear least-squares curve-fitting method.[22] For each host−guest pair examined, the plot of F as a function of $[G]_0$ gave an excellent fit, verifying the validity of the 1:1 inclusion complexation stoichiometry assumed. Additionally, Job plots also showed the 1:1 complexation stoichiometries by calculating the host−guest CT band (Figure S10, Supporting Information). The K_a data are listed in Table 1. As expected, the association constants for the formation of [2]pseudorotaxanes and/or external complexes with CP5A in the aqueous buffer solution are significantly greater than those observed for native P5A. For example, the K_a values for $\mathbf{1}^{2+}$, $\mathbf{4}^{2+}$, and $\mathbf{6}^{2+}$ with the anionic host are dramatically increased by factors of 2400, 900, and 950, respectively, compared with those with native P5A in DMSO.[17a] The very strong complexes formed between the 1,4-bis(pyridinium)butanes and CP5A further demonstrate that the electrostatic interactions[23] between negative carboxylate groups and positive bis(pyridinium) groups, and hydrophobic interactions between the aliphatic chain (or pyridinium ring) and the host cavity play more important role than cation−π-electron interactions[17] and [C−H···π] interactions[18e] in the present inclusion complexation.

As can be seen from Table 1, the association constants of all [2]pseudorotaxane-type complexes exceed 10^5 M^{-1}, which are enhanced by factors of 460, 150, 150, 290, and 100 for $\mathbf{1}^{2+}$⊂CP5A, $\mathbf{3}^{2+}$⊂CP5A, $\mathbf{4}^{2+}$⊂CP5A, $\mathbf{6}^{2+}$⊂CP5A, and $\mathbf{7}^{2+}$⊂CP5A, respectively, compared with that of external complex $\mathbf{5}^{2+}$⊂CP5A [$K_a = (2.4 \pm 0.3) \times 10^3$ M^{-1}] The highly effective binding of the [2]pseudorotaxanes is mainly due to the cooperative electrostatic interactions between two pyridinium cations of guest and two anionic portals of host. Furthermore, the stronger hydrophobic

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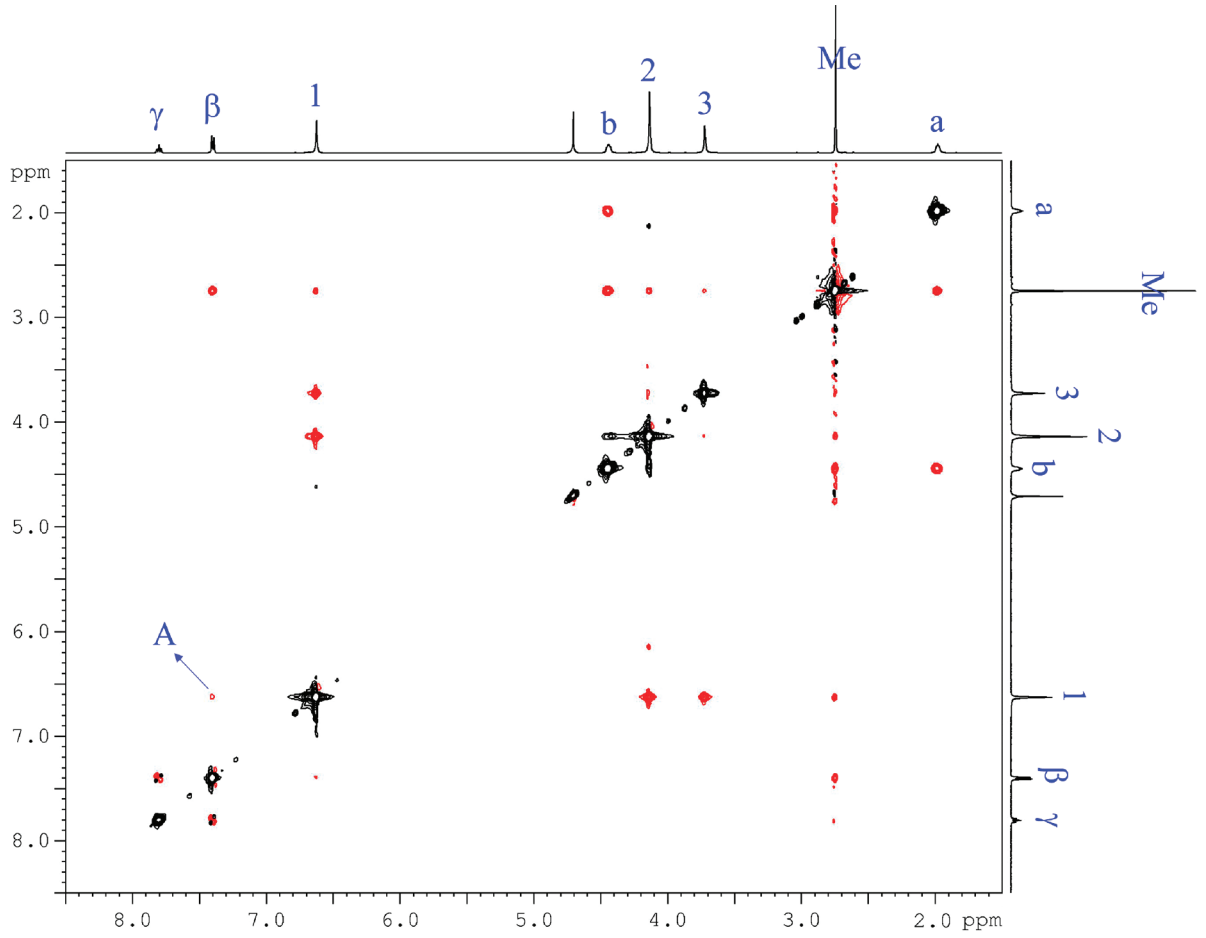

Figure 3. 2D ROESY analysis of $\mathbf{5}^{2+}$ with CP5A in D_2O with a mixing time of 200 ms (500 MHz, 298.15 K; the concentrations of host and guest are 5.5 and 5.0 mM, respectively).

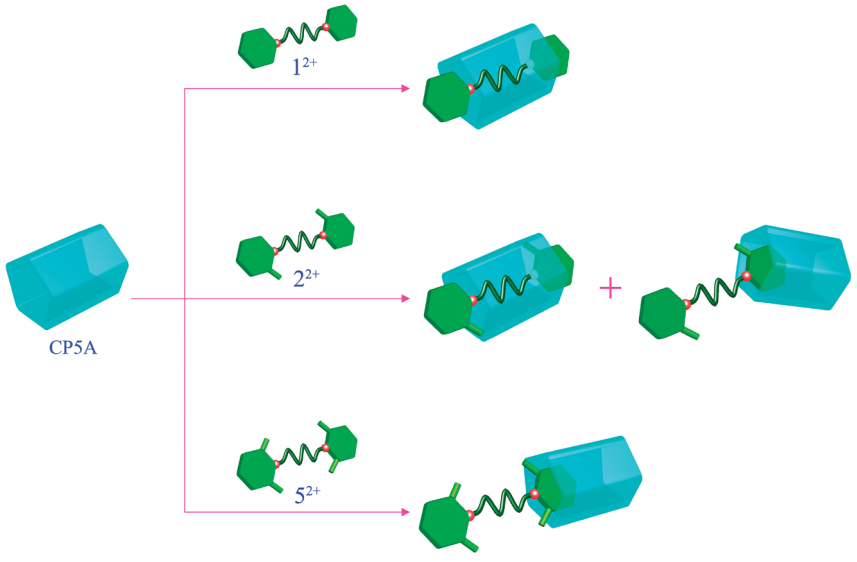

Figure 4. Possible geometry structures of host−guest complexes $\mathbf{1}^{2+}\subset$CP5A, $\mathbf{5}^{2+}\subset$CP5A, and $\mathbf{2}^{2+}\subset$CP5A.

interactions and [C−H···π] interactions of the aliphatic chain are another two possible reasons. Among the [2]pseudorotaxanes, $\mathbf{1}^{2+}\subset$CP5A gives the largest association constant, (1.1 ± 0.2) × 10^6 M^{-1}. The introduction of either electron-donating or electron-withdrawing groups decreases the K_a values. For example, although the CT absorptions of CP5A with $\mathbf{6}^{2+}$ and $\mathbf{7}^{2+}$,

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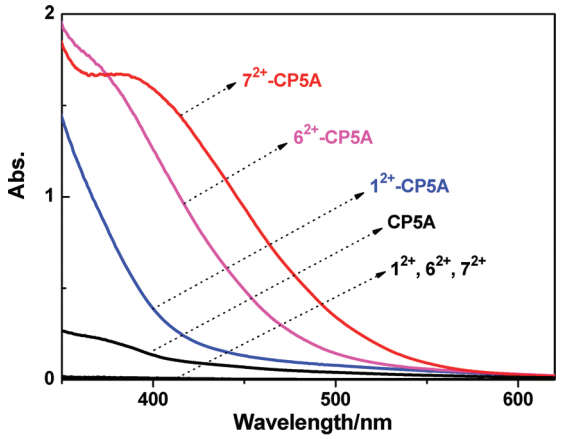


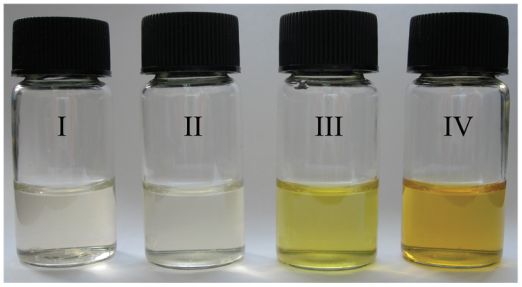


Figure 5. UV−vis spectra of 1^{2+}, 6^{2+}, and 7^{2+} (2.6−2.9 mM) in the presence of approximately 1 equiv of CP5A (2.9 mM) in pH 7.2 phosphate buffer solution at 298.15 K. Pictures showing the color changes of CP5A upon complexation with 1 equiv of guests (2.9 mM in pH 7.2 phosphate buffer solution): (I) free CP5A, (II) + 1^{2+}, (III) + 6^{2+}, and (IV) + 7^{2+}.

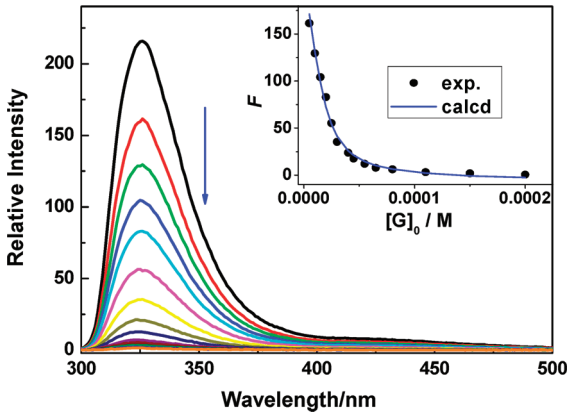


Figure 6. Fluorescence spectra of CP5A (4.11×10^{-5} mol·dm^{-3}) in the presence and absence of 7^{2+} in aqueous phosphate buffer solution (pH 7.2) at 298.15 K. Inset: the nonlinear least-squares analysis to calculate the association constant (K_a).

possessing electron-withdrawing pyridyl and COOEt, are very obvious and these two complexes can be observed visually (Figure 5), the association constants are reduced by factors of 1.6, and 4.6, respectively, compared with that of 1^{2+}. This demonstrates that the charge−transfer interaction is not a crucial driving force in the complexation of anionic CP5A with 1,4-bis(pyridinium)butane derivatives. Electrostatic and hydrophobic

Table 1. Association Constants K_a (M^{-1}) and Binding Geometries for the Host−Guest Complexation in Aqueous Phosphate Buffer Solution (pH 7.2) at 298.15 K

	K_a[a] (M^{-1})	binding geometry
1^{2+}	$(1.1 \pm 0.2) \times 10^6$	pseudorotaxane
2^{2+}	$(1.9 \pm 0.4) \times 10^4$	pseudorotaxane/external complex
3^{2+}	$(3.5 \pm 0.1) \times 10^5$	pseudorotaxane
4^{2+}	$(3.6 \pm 0.5) \times 10^5$	pseudorotaxane
5^{2+}	$(2.4 \pm 0.3) \times 10^3$	external complex
6^{2+}	$(7.0 \pm 0.7) \times 10^5$	pseudorotaxane
7^{2+}	$(2.4 \pm 0.2) \times 10^5$	pseudorotaxane

[a] Values are for Br^- salts in aqueous phosphate buffer solution (pH 7.2).

interactions should play great role in the present association process. The introduction of substituents results in an increase of steric hindrance, and that is why both the electron-withdrawing 4-pyridyl and COOEt groups (6^{2+}, 7^{2+}) and electron-donating CH_3 groups (3^{2+}, 4^{2+}) decrease the original binding ability. For 3^{2+} and 4^{2+}, another possible reason may be the decreased charge-transfer interactions between host's dialkoxybenzene and guest's pyridinium ring due to the electron-donating effects of methyl groups. On the other hand, guest 6^{2+} gives a larger K_a value than 7^{2+}. One reasonable reason was that there are additional C−H$\cdots\pi$ interactions between host's methylenes (H_2) and guest's 4-pyridyl groups. It is worthy to note that, these results are entirely different with P5A/1,4-bis(pyridinium)butane and dibenzo-24-crown-8/1,2-bis(pyridinium)ethane systems[17a,21] in organic solvents. In the later two cases, the charge-transfer interactions are very important and the electronic nature of the guests' substituents dramatically affects the molecular recognition behavior, where the introduction of electron-withdrawing groups to bis(pyridinium) guests would generally result in efficient chromophoric sensor behavior and improved complexation, and vice versa.

CONCLUSION

In summary, we have demonstrated the binding behavior of the negatively charged CP5A with 1,4-bis(pyridinium)butane derivatives. The results obtained indicate undoubtedly the formation of [2]pseudorotaxanes and/or external geometries, where the electrostatic interaction between negative carboxylate groups and positive pyridinium groups significantly reinforces the complex stability. The position of the substituents attached to the pyridinium rings in 1,4-bis(pyridinium)butane dramatically affects the binding affinities and the binding modes. (i) For the 3- or 4-substituted guests, not only are the [2]pseudorotaxane-type complexes formed, but also the very large K_a values are given (>10^5 M^{-1}). (ii) For the bulky 2,6-dimethyl-substituted guest 5^{2+}, an external complex is formed and the binding ability is reduced more than 100 times, compared with [2]pseudorotaxanes. (iii) Both of the binding geometries and a moderate K_a value are found for 2^{2+}, having one methyl group in the 2-position of pyridinium ring. Although the introduction of electron-withdrawing groups dramatically enhances the CT absorptions, making the [2]pseudorotaxanes $6^{2+}\subset$CP5A and $7^{2+}\subset$CP5A colored from light yellow to yellow, their association constants are reduced. This also indicates that the driving force of anionic CP5A are very different with the native P5A. Electrostatic and hydrophobic interactions, instead of the charge-transfer interaction,

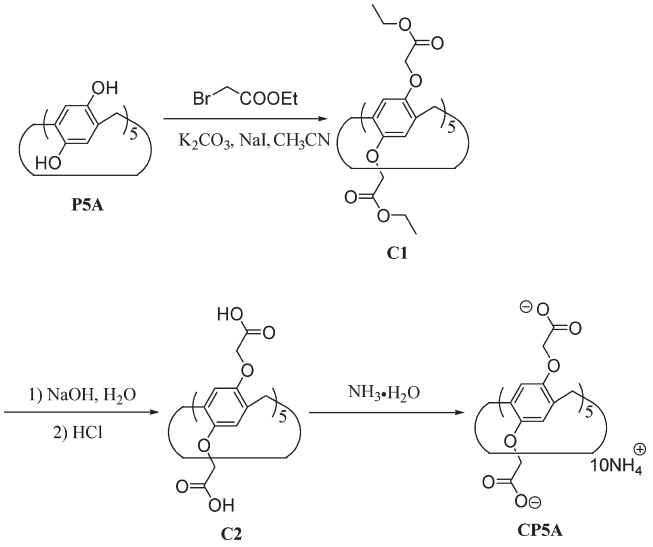
play crucial role in the binding between CP5A and 1,4-bis-(pyridinium)butane cations in aqueous media. The present highly effective complexation would find applications of the efficient fabrication of mechanically interlocked structures and large supramolecular systems.

EXPERIMENTAL SECTION

General Experimental Procedures. UV−vis spectra were recorded in a conventional 1 cm path (1 × 0.25 cm) quartz cell on a UV spectrophotometer equipped with a temperature controller to keep the temperature at 25 °C. Fluorescence titrations were measured in a conventional rectangular quartz cell (10 × 10 × 45 mm^3) with the excitation and emission slits at a width of 5 nm, which was kept at 25 °C through a temperature controller. The excitation wavelengths for CP5A were 290 nm. ^{1}H NMR, ^{13}C NMR, and 2D ROESY spectra were recorded on a 500 M Hz NMR instrument.

Materials. Starting materials were commercially available unless noted otherwise. The phosphate buffer solution of pH 7.2 was prepared by dissolving disodium hydrogen phosphate (25.79 g) and sodium dihydrogen phosphate (4.37 g) in distilled, deionized water (1000 mL) to make a 0.1 mol dm^{-3} solution. The pH value of the buffer solution was verified on a pH-meter calibrated with two standard buffer solutions. All the bis(pyridinium) dibromide salts (**1**·2Br−**7**·2Br) were prepared by literature methods and recrystallized and dried under reduced pressure before use.[9b,24] CP5A was prepared by a slight modification of the reported procedure.[18b]

Slight Modification of CP5A Synthesis



Ethoxycarbonyl-Substituted P5A (C1). P5A (1.22 g, 2.00 mmol) was dissolved in 50 mL CH_3CN, and K_2CO_3 (3.31 g, 24.0 mmol) was added. The reaction mixture was stirred for 0.5 h, and then a small amount of NaI (20.0 mg) and excess of ethyl bromoacetate (8.35 g, 50.0 mmol) was added. The solution was heated to reflux for 15 h. The cooled reaction mixture was filtered and washed with chloroform. The filtrate was removed under vacuum, and the residue was further purified by crystallization by slow diffusion of methanol into a chloroform solution. The product was collected by filtration, washed with methanol, and dried under vacuum (C2, 1.18 g, yield 40%).

Carboxylic Acid Substituted P5A (C2). A solution of C1 (0.30 g, 0.20 mmol) in THF (40 mL) was treated with 20% aqueous sodium hydroxide (10 mL) at reflux for 10 h. The mixture was concentrated under reduced pressure, diluted with water (10 mL), and acidified with HCl. The precipitated product was collected by filtration, washed with water, and dried under vacuum (C2, 203 mg, yield 85%).

Carboxylatopillar[5]arene (CP5A). C2 (200 mg, 0.168 mmol) was placed into 20 mL of methanol/water (1: 1, v: v) and ammonium hydroxide (30.7 mg, 1.80 mmol) was added. The mixture was stirred for 4 h and then concentrated. The product was recrystallized using water and methanol and dried under vacuum (CP5A, 202 mg, yield 88%).

ASSOCIATED CONTENT

Supporting Information. NMR spectra of CP5A and guests, Job plots, and other data as described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) The nonlinear curve-fitting was based on the following equation: $F = I_0 - (0.5\alpha((H_0/2 + G_0 + (1/K_a)) - (((H_0/2 + G_0 + (1/K_a))-(H_0/2 + G_0 + (1/K_a)) - 4H_0/2G_0)^{1/2})))$ where F is the fluorescence intensity of host at $[G]_0$, $[H]_0$ is the fixed initial concentration of the host, and $[G]_0$ is the initial concentration of G. Typical curve-fitting plots are shown in Figure 6. The results are summarized in Table 1.

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