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Complexation of Racemic 2,6-Helic[6]arene and Its Hexamethyl-Substituted Derivative with Quaternary Ammonium Salts, *N*-Heterocyclic Salts and Tetracyanoquinodimethane

Geng-Wu Zhang,[a],[b] Peng-Fei Li,[a] Han-Xiao Wang,[a],[b] Ying Han,[a] and Chuan-Feng Chen*[a],[b]

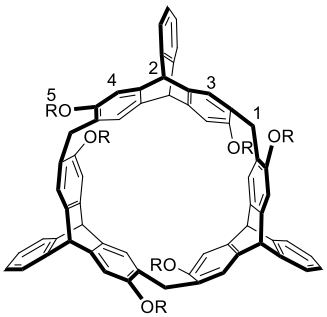
Dedication ((optional))

Abstract: The complexation of racemic 2,6-helic[6]arene **1** and its hexamethyl-substituted derivative **2** with quaternary ammonium salts, *N*-heterocyclic salts and tetracyanoquinodimethane were described in details. It was found that host **2** could form stable complexes with acetyl choline, thiaacetyl choline, *N*,*N*,*N*-trimethylbenzenammonium salt, pyridinium and 4,4'-bipyridinium salts in solution and/or in the solid state. The unsubstituted macrocycle **1** showed more significant complexation with the widely tested quaternary ammonium salts and *N*-heterocyclic salts, and exhibited stronger complexation towards the guests than its derivative **2**. Moreover, it was found that macrocycle **1** and its derivative **2** could also complex with neutral electron-deficient tetracyanoquinodimethane (TCNQ), and the association constants were determined to be 2840±94 and 1358±46 M^{-1}, respectively. These results could make this new macrocycle and its derivatives find wide applications in the design and construction of functional supramolecular assemblies.

Introduction

Host-guest chemistry[1] has been a topic of great interest during the past decades since the cation-complexing property of the crown ether was first reported by Pedersen.[2] Undoubtedly, macrocyclic hosts play key roles in host-guest chemistry, and the development of novel macrocyclic hosts with the capabilities of binding different kinds of substrates has always been one of the most important topics in this research area.[3] Macrocyclic arenes including calixarenes,[4] resorcinarenes,[5] cyclotriveratrylenes,[6] pillararenes,[7] and their analogues[8] have become one kind of the most extensively studied synthetic macrocyclic hosts for their potential applications in the fields of biology,[4c, 9] environment,[10] and materials science.[11] Moreover, various supramolecular assemblies such as rotaxanes, catenanes and vesicles based on these macrocyclic arenes could also be constructed and applied in supramolecular catalysis,[12] sensors[13] and supramolecular polymers.[14]

Triptycene[15] and its derivatives are a kind of aromatic molecules with arene units fused *via* a [2.2.2]bicycle-octatriene bridgehead system. The unique rigid three-dimensional structures enable them to be widely applied in supramolecular chemistry,[16] synthetic molecular machines,[17] materials science[18] and other research areas.[19] Recently, we reported a novel macrocyclic arene named 2,6-helix[6]arene, which was composed of three chiral triptycene moieties, and had a hex nut-like structure with a helical chiral cavity and highly fixed conformation.[20] The crystal structure showed that the macrocycle had a large cavity which could be compared to that of pillar[6]arene,[21] β-cyclodextrin[22] or cucurbit[7]uril.[23] It could be deduced that this macrocyclic host with the large and electron-rich cavity would exhibit complexation properties towards a wide range of guests, especially electron-deficient guests, which would be important in exploring functional applications of this new macrocyclic host and its derivatives. Herein, we report the complexation properties of racemic 2,6-helic[6]arene **1** and its hexamethyl-substituted derivative *rac*-**2** (Figure 1) in details. It was found that the host *rac*-**2** showed significant complexation with quaternary ammonium salts and *N*-heterocyclic salts in both solution and in the solid state. Moreover, we found that unsubstituted host *rac*-**1** exhibited even stronger complexation towards the widely tested guests (Figure 2) than its derivative *rac*-**2** probably due to the extra non-covalent interactions between host *rac*-**1** and the guests. Additionally, it was also found that *rac*-**1** and its derivative *rac*-**2** could complex with TCNQ, and the association constants were determined to be 2840±94 and 1358±46 M^{-1}, respectively.



rac-**1** R = H; *rac*-**2** R = Me

Figure 1. Structures and proton designations of racemic 2,6-helic[6]arene **1** and its derivative *rac*-**2**.

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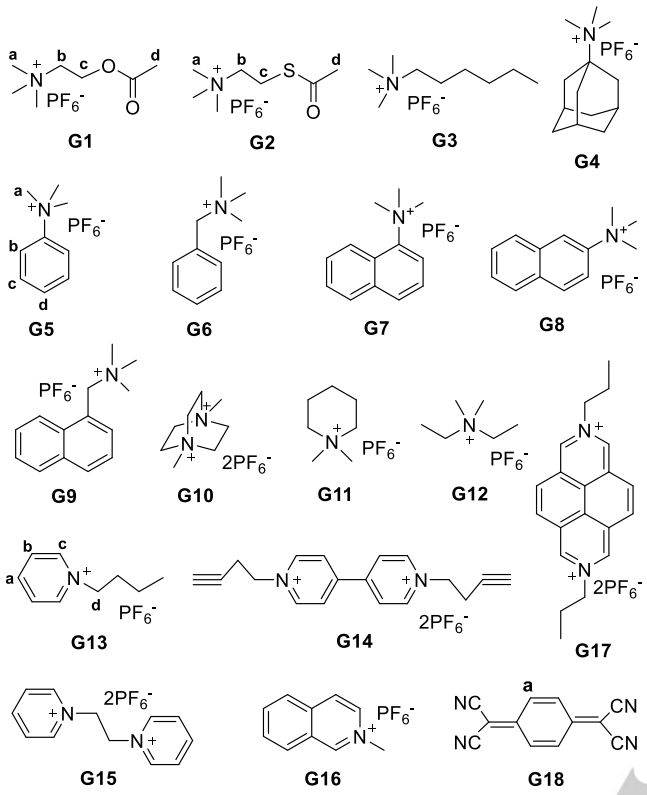

Figure 2. Structures and proton designations of the tested guests **G1**-**G18**.

Results and Discussion

Complexation between host *rac*-2 and acetyl choline, thiaacetyl choline and *N*,*N*,*N*-trimethylbenzeneammonium salt. Acetyl choline and its derivatives were a class of trimethylamine-group-containing compounds with important biological activities, which have attracted much attention during the past three decades.[24] In 1990, Dougherty and his group reported a synthetic host comprising primary aromatic rings, which showed strong affinity towards acetyl choline, and predicted that the cation-π interaction played an important role in the formation of the complex.[24a] In 1997, Aoki group reported the first single crystal of host-guest complex between acetyl choline and the macrocyclic host, and demonstrated the multiple cation–π interactions could effectively stabilize the complex.[24b]

In 2,6-helic[6]arene and its derivatives, six benzene rings formed a pre-organized hexagonal cavity with fixed conformation, so we deduced that they could facilitate the binding of cationic guests with collaborative cation-π and other multiple non-covalent interactions.[25] Therefore, we firstly investigated the complexation ability of the hexamethyl-substituted macrocycle *rac*-**2** with acetyl choline **G1** in solution by ^{1}H NMR spectroscopy. As shown in Figure 3，when equivalent *rac*-**2** and guest **G1** were mixed in 1:1 (*v*/*v*) $CDCl_3$/acetone-d_6 (2.00 mM), the ^{1}H NMR spectrum showed a distinctive difference from that of free *rac*-**2** and guest **G1**, which demonstrated the formation of the complex. The proton signals of *rac*-**2** all downfield shifted to some extent, but the signals of the trimethylamino proton H_a and the two methylene protons H_b and H_c were difficult to distinguish. Through gradually adding guest **G1** into the solution of *rac*-**2**, the complexation-induced broadened signals of protons H_a, H_b, and H_c were assigned and found to exhibit significant upfield shifts, while the acetyl proton H_d of the guest showed a relatively small downfield shift ($\Delta\delta$ = -0.05 ppm). These observations suggested that in the complexation between *rac*-**2** and **G1**, the trimethylamino group of the guest was located inside the cavity of the macrocycle, and acetyl group might be outside of the cavity. Moreover, molar ratio plot based on the ^{1}H NMR titration data showed the complexation between *rac*-**2** and guest **G1** was in a 1:1 mode. In the same tested conditions, *rac*-**2** with acetyl thiocholine **G2** showed similar complexation behavior to that in complex *rac*-**2**·**G1** and formed 1:1 complex *rac*-**2**·**G2** (Figure S40). According to the ^{1}H NMR titration experiments, the association constants K_a of complexes *rac*-**2**·**G1** and *rac*-**2**·**G2** were calculated to be (5.30±0.59)×10^2 and (1.67±0.25)×10^3 M^{-1}, respectively, by using a nonlinear curve fitting method.[26] The electrospray ionization mass spectra (ESI-MS) also confirmed the formation of 1:1 complexes between host *rac*-**2** and guests **G1** and **G2**, in which the strong *m/z* peaks at 1125.51 and 1140.49 corresponding to the positively charged species [*rac*-**2**·**G1**-PF_6] and [*rac*-**2**·**G2**-PF_6] were observed, respectively.

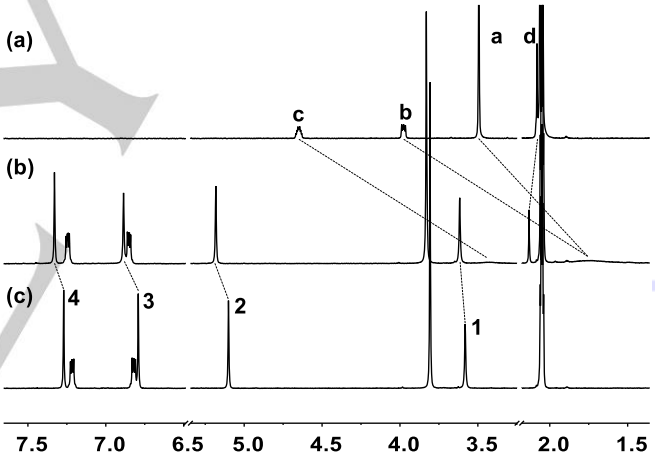

Figure 3. Partial ^{1}H NMR spectra (400 MHz, 298 K, 1:1 v/v $CDCl_3$/acetone-d_6) of (a) free guest **G1**, (b) *rac*-**2** with 1.0 equiv. guest **G1**, (c) free *rac*-**2**. [*rac*-**2**]$_0$ = 2.00 mM.

The single crystals of host *rac*-**2** could be easily obtained by the evaporation of its CH_2Cl_2 solution. Similar to macrocycle *rac*-**1**,[20] *rac*-**2** also had a hexagonal prism cavity surrounded by six benzene rings belonging to the three triptycene moieties, and the distances between the two centers of opposite aromatic faces were 8.73, 9.05, and 9.45 Å, respectively (Figure 4). By slow evaporation of the solution of *rac*-**2** and guest **G2** in CH_2Cl_2, we also obtained the crystal of complex *rac*-**2**·**G2** suitable for X-ray diffraction analysis. As shown in Figures 4c and 4d, guest **G2** was encapsulated in the cavity of *rac*-**2** to form a 1:1 complex, and the trimethylamino group was located in the center of the cavity. The distances between the nitrogen atom of **G2** and the benzene rings of *rac*-**2** were 4.45, 4.46, 4.56, 4.58, 4.59, and 4.65 Å, respectively. Besides, multiple C-H···π interactions

between the protons of trimethylamino group and the aromatic rings of the host were found, and the distances between the protons of the guest and the aromatic rings of the host were from 2.76 to 2.88 Å. Moreover, there also existed one C-H···S hydrogen bond (2.96 Å) between the methoxyl proton and the sulfur atom of the guest. These multiple non-covalent interactions played an important role in the formation of the complex. To our knowledge, this was the first crystal structure of host-guest complex with trimethylamino group of thiaacetyl cholines fully encapsulated in the cavity of the host.

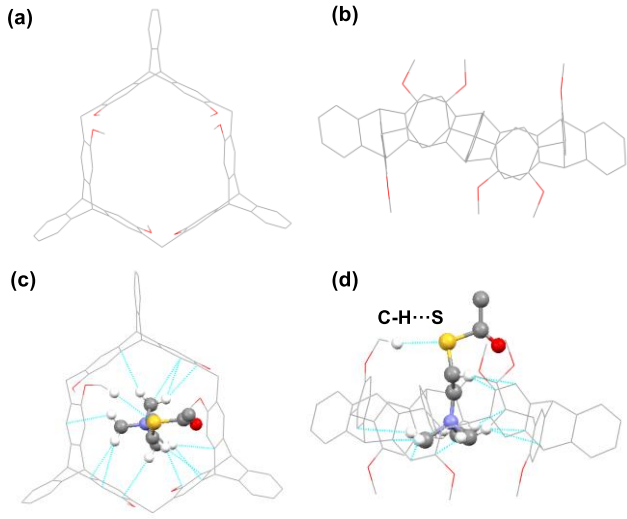

Figure 4. (a) Top view and (b) side view of crystal structure of *rac*-**2**. (c) Top view and (d) side view of crystal structure of complex *rac*-**2**·**G2**. PF_6^- counterion and hydrogen atoms not involved in the noncovalent interactions are omitted for clarity.

We also tested the complexation between host *rac*-**2** with *N*,*N*,*N*-trimethylbenzeneammonium salt **G5** in solution by ^{1}H NMR spectroscopy. Similar to the cases of **G1** and **G2**, *rac*-**2** could also form 1:1 stable complex with guest **G5**. And from the ^{1}H NMR spectra, it could be seen that the protons H_a and H_b of the guest exhibited significant upfield shifts, while the protons H_c and H_d showed relatively small downfield shifts, which indicated that the trimethylamino group was located inside the cavity of the host. Moreover, the association constant K_a of complex *rac*-**2**·**G5** was calculated to be (3.05±0.26)×10^3 M^{-1}, obviously larger than those of host *rac*-**2** with **G1** and **G2**, which might be due to the additional non-covalent interactions between the benzene ring of guest **G5** and the host.

Complexation between host *rac*-2 and pyridinium and 4,4'-bipyridinium salts. It was known that pyridinium salts and bipyridinium salts not only were used as herbicides to play an important role in various biological systems, but also were used as some of the most common guests to be studied intensively in numerous inclusion complexes.[3a, 3b, 27] Thus, we first tested the complexation between host *rac*-**2** and pyridinium guest **G13** in solution by NMR spectroscopy (Figure 5). It was found that the complexation between host *rac*-**2** and guest **G13** was also a fast exchange process. The proton H_2 of the host was downfield shifted, whereas the protons H_a, H_b, H_c, H_d of the pyridinium ring showed upfield shifts, which could be attributed to their positions in the shielding region of the aromatic rings of host *rac*-**2**. The stoichiometry of this complex was determined to be 1:1 by a mol ratio plot, and the association constant K_a for the complex was calculated to be 109±8 M^{-1}, by using a nonlinear curve fitting method.

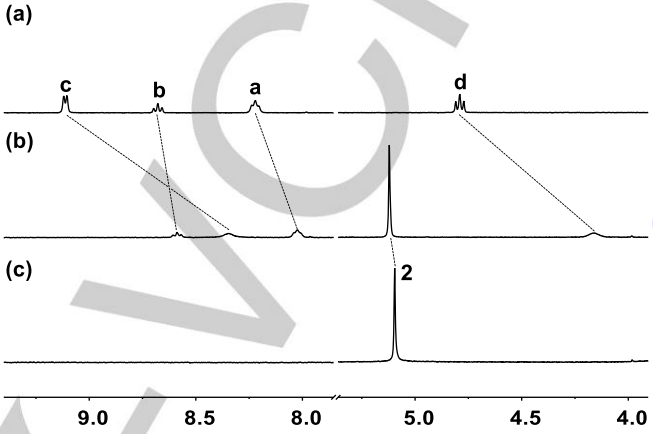

Figure 5. ^{1}H NMR spectra (400 MHz, 298 K, 1:1 *v/v* $CDCl_3$/acetone-d_6) of (a) free guest **G13**, (b) *rac*-**2** + 1.0 equiv. **G13**, (c) free *rac*-**2**. [*rac*-**2**]$_0$ = 2.00 mM.

We also obtained single crystals suitable for X-ray diffraction analysis from a CH_2Cl_2 solution of *rac*-**2** and **G13**. As shown in Figure 6, the pyridinium ring was in the center of the cavity and the distances between the nitrogen atom of the guest and the benzene rings of the host were 4.23, 4.38, 4.62, 4.71, 4.80, 4.94 Å, respectively. C-H···π interactions between the aliphatic protons of guest **G13** and the benzene rings of the host with the distances of 2.90 (A), 2.88 (B), 2.84 (C), 2.84 (D), and 2.75 Å (E), respectively, were observed. Moreover, multiple C–H···F hydrogen bonding interactions between the hexafluorophosphate group and the host and the pyridinium ring of **G13** with the distances of 2.50 (a), 2.58 (b), 2.29 (c) and 2.51 Å (d), respectively, could be found as well. These multiple intermolecular interactions played an important role in the formation of the complex.

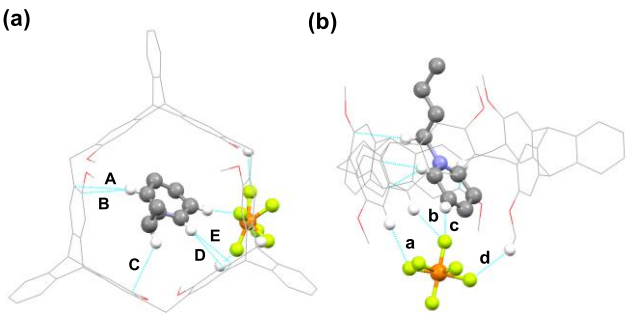

Figure 6. (a) Top view and (b) side view of crystal structure of *rac*-**2**·**G13**. Hydrogen atoms not involved in the noncovalent interactions were omitted for clarity.

Similar to the case of **G13**, 4,4'-bipyridinium guest **G14** could also form 1:1 complex with macrocycle *rac*-**2** in solution, and the association constant was calculated to be 34±2 M^{-1}. Moreover, the strong *m/z* peak of positively charged species [*rac*-**2**·**G14**-PF_6] was observed in ESI-MS (Figure S112), which further supported the formation of the 1:1 complex.

Complexation between host *rac*-1 and the quaternary ammonium guests. Compared with *rac*-**2**, macrocycle *rac*-**1** without any modification has more orderly structure and better solubility in acetone. Therefore, we also tested its complexation abilities with the guests **G1** and **G2**.

When *rac*-**1** (2.00 mM) with 1.0 equivalent of **G1** were mixed in acetone-d_6, the ^{1}H NMR spectrum exhibited a very different set from signals to those of free *rac*-**1** and guest **G1** (Figure 7). Similar to the case of *rac*-**2**·**G1**, only one new set of signals were observed, indicating a fast-exchange complexation between *rac*-**1** and **G1**. Signals of protons H_a, H_b, and H_c close to the trimethylamino group in the guest exhibited significant upfield shifts ($\Delta\delta$ = -1.73, -2.21, -1.20 ppm, respectively), while the acetyl proton H_d showed relatively small downfield shift ($\Delta\delta$ = -0.05 ppm). The proton signals of *rac*-**1** were all downfield shifted to some extent. Complexation-induced broadened signals for protons H_a, H_b and H_c of the guest were also observed. These observations suggested that in the complexation between *rac*-**1** and **G1**, the trimethylamino group of the guest was also located inside the cavity of macrocycle. Moreover, molar ratio plot based on the ^{1}H NMR titration data showed the complexation between *rac*-**1** and guest **G1** was in a 1:1 mode and the association constant was calculated to be (3.53±0.45)×10^3 M^{-1}, which was obvious larger than that of complex *rac*-**2**·**G1**. Under the same tested conditions, host *rac*-**1** with acetyl thiocholine **G2** showed similar complexation behavior to that of complex *rac*-**1**·**G1** (Figure S8), and formed 1:1 complex with the association constant of (4.76±0.72)×10^3 M^{-1}.

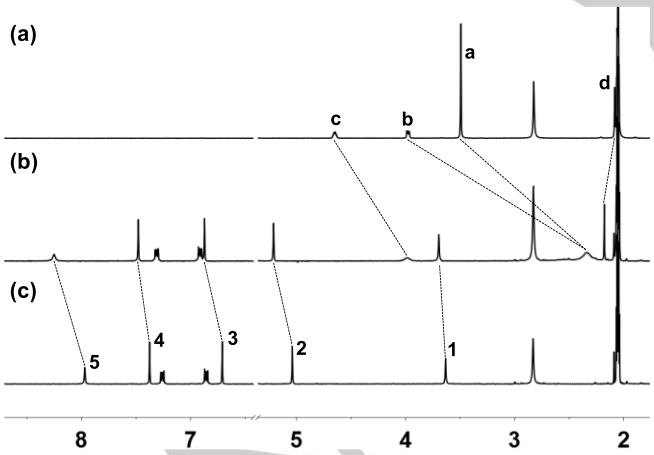

Figure 7. Partial ^{1}H NMR spectra (500 MHz, 298 K, acetone-d_6) of (a) free guest **G1**, (b) *rac*-**1** with 1.0 equiv. guest **G1**, (c) free *rac*-**1**. [*rac*-**1**]$_0$ = 2.00 mM.

Since stronger complexation between host *rac*-**1** and guests **G1**-**G2** than that of host *rac*-**2** and the guests were observed, we further explored the complexation of host *rac*-**1** and a series of quaternary ammonium guests **G3**-**G12** in details, and the results were summarized in Table 1.

Table 1. Association constants K_a for 1:1 complexation of *rac*-**1** and the guests at 298 K.

guest	solvent	K_a (M^{-1})	ΔG (kJ/mol)[a]
G1	acetone-d_6	(3.53±0.45)×10^3	-20.24
G2	acetone-d_6	(4.76±0.72)×10^3	-20.98
G3	acetone-d_6	(8.66±0.79)×10^3	-22.46
G4	acetone-d_6	(7.94±0.24)×10^3	-22.25
G5	acetone-d_6	(1.33±0.14)×10^4	-23.53
G6	acetone-d_6	(1.15±0.03)×10^4	-23.17
G7	acetone-d_6	(1.34±0.01)×10^3	-17.84
G8	acetone-d_6	(8.66±0.50)×10^3	-22.46
G9	acetone-d_6	(3.76±0.14)×10^2	-14.69
G10	CD_3CN	(1.68±0.06)×10^3	-18.40
G11	acetone-d_6	(6.10±0.24)×10^3	-21.59
G12	acetone-d_6	(5.29±0.11)×10^3	-21.24
G13	acetone-d_6	(1.82±0.16)×10^3	-18.60
G14	acetone-d_6	(9.64±0.23)×10^2	-17.02
G15	CD_3CN	(2.04±0.22)×10^2	-13.18
G16	acetone-d_6	62±8	-10.23
G17	CD_3CN	(4.73±0.29)×10^2	-15.26

[a] The free energies of dissociation (ΔG) were calculated from the K_a values by using the expression $\Delta G = -RTlnK_a$.

Similar to the cases of **G1** and **G2**, the quaternary ammonium guests **G3** and **G4** could also form 1:1 stable complexes with host *rac*-**1** in solution. The association constants of the 1:1 complexes were calculated to be (8.66±0.79)×10^3 and (7.94±0.24)×10^3 M^{-1}, respectively. Compared with the alkyl substituted guests **G1**-**G4**, host *rac*-**1** showed stronger binding abilities with the aromatic substituted guests **G5** and **G6** perhaps due to the additional π-π interactions between the aromatic rings of the host and the guests. As for *N*,*N*,*N*-trimethylnaphthalen-1-aminium salt **G7** and its isomer **G8**, they could also form 1:1 complexes with host *rac*-**1**, and the association constants K_a of the complexes were calculated to be (1.34±0.01)×10^3 and (8.66±0.50)×10^3 M^{-1}, respectively, which were larger than that of the naphthylmethyl substituted quaternary ammonium salt **G9** with host *rac*-**1**. The difference in the association constants might be due to the steric hindrance between the naphthalene ring and the host molecule. Similarly, it was found that host *rac*-**1** also had strong binding affinities towards quaternary ammonium salts **G10**, **G11** and **G12**, and the association constants were found to be (1.68±0.06)×10^3, (6.10±0.24)×10^3 and (5.29±0.11)×10^3 M^{-1}, respectively.

Moreover, the ESI mass spectra provided further evidence for the formation of the complexes. As a result, the strong peak at *m/z* 1040.4 for [*rac*-**1**·**G1**-PF_6]$^+$ was found by testing a solution

of *rac*-**1** and **G1** in acetone, which supported the formation of the 1:1 complex. Similarly, the strong peaks for the formation of the complexes between host *rac*-**1** and guests **G2**-**G12** were also observed under the same tested conditions (Figure S91–S101).

Complexation between host *rac*-1 and the *N*-heterocyclic salts. We further tested the complexation between host *rac*-**1** and pyridinium salt **G13** in solution by NMR spectroscopy. It was found that the complexation between host *rac*-**1** and guest **G13** was also a fast exchange process. The protons H_1, H_2, and H_5 of the host showed downfield shift, whereas the protons H_a, H_b, H_c, and H_d of the guest all shifted upfield, which could be attributed to their positions in the shielding region of the aromatic rings of host *rac*-**1** (Figure 8). The stoichiometry of complex *rac*-**1·G13** was determined to be 1:1 by a mol ratio plot, and the association constant for the complex was calculated to be $(1.82\pm0.16)\times10^3$ M^{-1} by using a nonlinear curve fitting method. Moreover, it was found that host *rac*-**1** also showed obvious complexation with bipyridinium salt **G14** and 1,2-bis(pyridium)thane **G15**, and the association constants for the 1:1 complexes *rac*-**1·G14** and *rac*-**1·G15** were calculated to be 964±23 and 204±22 M^{-1} (Figures S73, S75), respectively. The smaller K_a values than that of complex *rac*-**1·G13** might resulte from the weak π-π stacking interactions between the macrocycle with a large cavity and rigid structure and the electron deficient guests **G14** and **G15**. Similarly, we found that quinoline salt **G16** and diazapyrenium guest **G17** also formed 1:1 complexes with *rac*-**1**, and the association constants K_a were 62±8 and 473±29 M^{-1} (Figures S77, S79), respectively.

ESI mass spectrometry was further used to characterize the complexes between host *rac*-**1** and guests **G13-G17**. Thus, the strong peak at *m*/*z* 1030.4 for [*rac*-**1·G13**–2PF_6]$^+$ was found with a solution of *rac*-**1** and **G13** in acetone as the sample, which provided another piece of evidence for formation of the 1:1 stable complex between host *rac*-**1** and guest **G13**. Similarly, formation of the 1:1 stable complexes between host *rac*-**1** and guests **G14**, **G15**, **G16** and **G17** was also supported by the ESI mass spectra, in which strong peaks at *m*/*z* 578.2, 540.2, 1038.4 and 592.2 for [*rac*-**1·G14**–2PF_6]$^{2+}$, [*rac*-**1·G15**–2PF_6]$^{2+}$, [*rac*-**1·G16**–2PF_6]$^+$ and [*rac*-**1·G17**–2PF_6]$^{2+}$, respectively, were observed (Figures S103–S106).

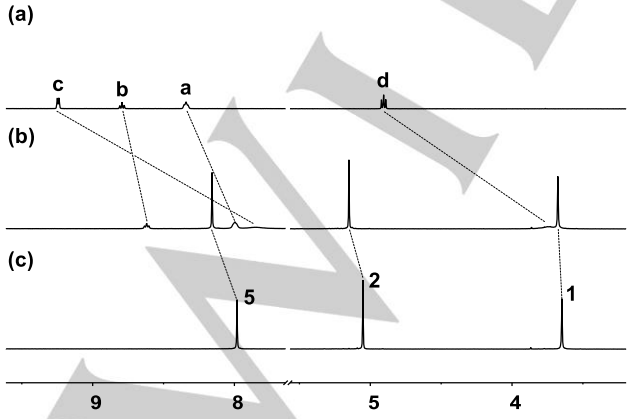

Figure 8. Partial ^{1}H NMR spectra (400 MHz, 298 K, acetone-d_6) of (a) free guest **G13**, (b) *rac*-**1** + 1.0 equiv. **G13**, (c) free *rac*-**1**. [*rac*-**1**]$_0$ = 2.00 mM.

Computational study between host *rac*-1 and the guests. In order to explore the complexation mode and gain further insights into the structural characteristics of the complexes formed by host *rac*-**1** and the guests in solution, DFT calculations of the free host *rac*-**1**, the free guests **G2** and **G13** chosed as the representatives and their complexes solvated in acetone solvent were then carried out at the B3LYP/6-31G level.

From the ESPs of the free host *rac*-**1** as shown in Figure 9a and 9b, it was found that the benzene rings surrounding the cavity of the host were electron-rich, while the ESPs of the free guests showed that the N atoms of **G2** and **G13** were electron-poor (Figure 9c and 9d). Therefore, it was easy to deduce that the N atoms of the guests would locate in the center of the cavity of the host through electrostatic interaction in the host-guest complexes. Moreover, the structures of the complexes *rac*-**1·G2** and *rac*-**1·G13** were also simulated in acetone (Figures S115). The relative Gibbs free energies were calculated to be -26.56 and -18.13 kJ/mol, respectively, which were consistent with the experimental results. It was further found that in the complex *rac*-**1·G2**, the Mulliken atomic charges of the host and the guest were 0.9084 and 0.0916, respectively. The Mulliken atomic charges of the host and the guest in the complex *rac*-**1·G13** were 0.8760 and 0.1240, respectively. These results indicated that partial positive charges were transfered from the guests to the host in the formation of the complexes.

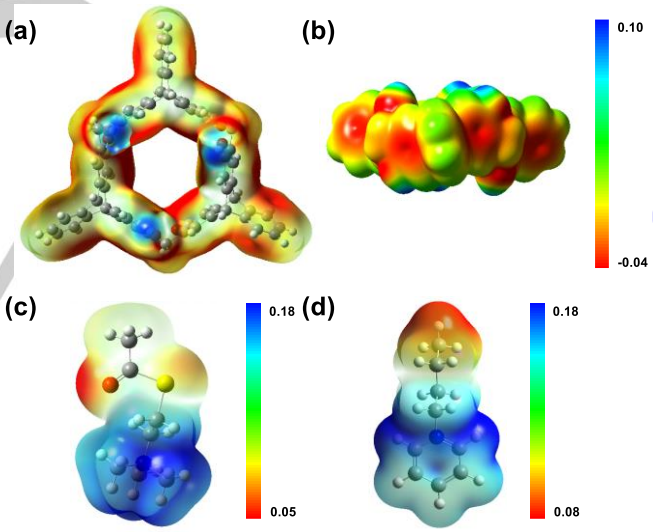

Figure 9. ESPs mapped onto electron density isosurfaces (ρ = 0.01) for (a) top view and (b) side view of calculated structure of *rac*-**1,** (c) **G2** and (d) **G13**.

Complexation between hosts *rac*-1 and *rac*-2 and TCNQ. TCNQ is a neutral electron-poor compound, so we also tested its complexation with hosts *rac*-**1** and *rac*-**2**. As shown in Figure 10b, when guest **G18** was added into the $CDCl_3$ solution of 1.0 equivalent *rac*-**2**, the NMR spectra showed that both complexed and uncomplexed signals were observed, which indicated a slow-exchange complexation. Proton H_a of the guest showed strikingly upfield shifted (Δδ = -2.91 ppm), which might be due to the strong shielding effect of the macrocycle. Besides, the proton signals of host *rac*-**2** were all shifted downfield. Moreover,

a peak at *m*/*z* = 1182.4 for *rac*-**2**·**G18** was also observed, indicating the formation of the 1:1 complex *rac*-**2**·**G18**. The association constant K_a of *rac*-**2**·**G18** was further calculated to be 1358±46 M^{-1} by the integration from a 1 : 1 mixture using the ^{1}H NMR single point method.[28]

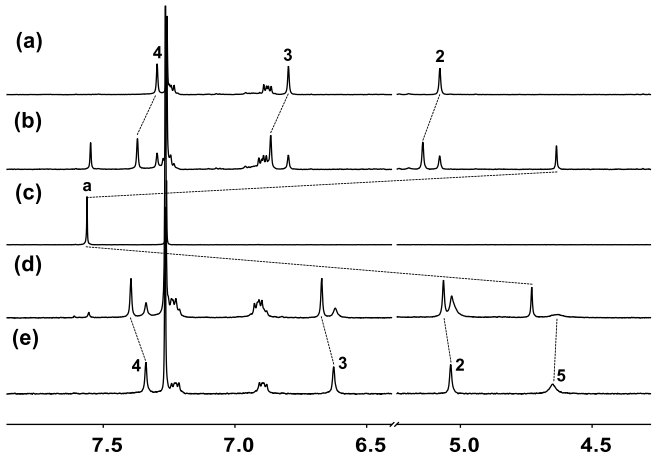

Figure 10. Partial ^{1}H NMR spectra (400 MHz, 298 K, $CDCl_3$) of (a) free *rac*-**2**. (b) *rac*-**2** + 1.0 equiv. **G18**, (c) free guest **G18**, (d) *rac*-**1** + 1.0 equiv. **G18**, and (e) free *rac*-**1**. $[rac\text{-}\mathbf{1}]_0 = [rac\text{-}\mathbf{2}]_0 = 1.50$ mM.

To investigate the complexation between host *rac*-**2** and guest **G18**, the 2D ROESY NMR experiment was further carried out. The results showed that the cross-peaks were detected between the proton H_a of **G18** and protons H_3 and H_4 in the benzene ring of the host (Figure S114), which suggested that guest **G18** threaded the central cavity of host *rac*-**2** to form a 1:1 complex. Under the same tested conditions, it was also found that host *rac*-**1** with guest **G18** showed similar complexation behavior to that of *rac*-**2**·**G18** (Figure 10d), and formed a 1:1 complex *rac*-**1**·**G18** with the association constant of 2840±94 M^{-1}, which was larger than that of complex *rac*-**2**·**G18**. This result might be ascribed to the multiple hydrogen bonding interactions between the hydroxy groups of host *rac*-**1** and guest **G18**.

Conclusions

In conclusion, we have proved that hexamethyl-substituted 2,6-helic[6]arene *rac*-**2** could form 1:1 complexes with acetyl choline, thiaacetyl choline, *N*,*N*,*N*-trimethylbenzenammonium, pyridinium, and 4,4'-bipyridinium salts in solution and/or in the solid state. Especially, we found that the unsubstituted 2,6-helic[6]arene *rac*-**1** could show significant complexation with the widely tested quaternary ammonium salts and *N*-heterocyclic salts, and exhibited stronger complexation than those of its hexamethyl-substituted derivative. Moreover, it was found that racemic 2,6-helic[6]arene **1** and its derivative **2** could also complex with neutral electron-deficient TCNQ to form stable 1:1 complexes with the association constants of 2840±94 and 1358±46 M^{-1}, respectively. Besides, the large and electron-rich cavity, fixed conformation and easily functionalization of the 2,6-helic[6]arene, its complexation abilities towards different kinds of tested guests could make this new macrocyclic host find wide applications in the design and construction of various supramolecular assemblies with specific structures and properties, which are underway in our group.

Experimental Section

General: All reactions were carried out under argon using oven-dried glassware. TLCs were performed on silica gel GF_{254}; chromatograms were visualized with UV light (254 and 360 nm). Flash column chromatography was performed on 100-200 mesh silica gel. Melting points, taken on an electrothermal melting point apparatus, were uncorrected. Commercial reagents were used without further purification. Anhydrous solvents were dried from 4 Å molecular sieves. Hosts **1** and **2**,[20] guests **G1**-**G6**,[8b, 25, 29] **G10**-**G17**[16f, 28b, 29] were prepared according to the published procedures**.**

Synthesis of G7. To a mixture of 1-naphthylamine (720 mg, 5.0 mmol) and potassium carbonate (3.50 g, 25.0 mmol) in CH_3CN (50 mL) was added methyl iodide (2.85 g, 25.0 mmol), and the mixture was stirred under r.t. overnight. Then, the reaction mixture was filtered, and the filtrate was concentrated in vacuo. The residue was washed with ethyl ether several times. The chloride salt was dispersed in 30 mL acetone, which was then added saturated aqueous NH_4PF_6 solution until a clear solution was obtained. After the solution was further stirred for 4 hours, the solvent was evaporated off. A white solid was precipitated, filtrated, washed with water, and then dried to afford compound **G7** (1.02 g, total yield 61.0 %) as a white solid. M.p.: 145-146°C. ^{1}H NMR (500 MHz, acetone-d_6): δ 8.73 (d, *J* = 8.9 Hz, 1H), 8.33–8.23 (m, 3H), 7.89-7.80 (m, 1H), 7.76 (dt, *J* = 29.1, 7.9 Hz, 2H), 4.23 (s, 9H). ^{13}C NMR (125 MHz, acetone-d_6): δ 141.5, 136.1, 132.8, 130.9, 128.3, 126.9, 124.7, 124.1, 123.0, 120.0, 57.6. HRMS (ESI): *m/z* calcd for $[M\text{-}PF_6]^+$ $C_{13}H_{16}N^+$: 186.1342; found: 186.1341.

Synthesis of G8. To a mixture of 1-naphthylamine (720 mg, 5.0 mmol) and potassium carbonate (3.5 g, 25.0 mmol) in CH_3CN (50 mL) was added MeI (2.85 g, 25.0 mmol), and the mixture was stirred under r.t. overnight. Then, the reaction mixture was filtered, and the filtrate was concentrated in vacuo. The residue was washed with ethyl ether several times. The chloride salt was dispersed in 30 mL acetone, which was then added saturated aqueous NH_4PF_6 solution until a clear solution was obtained. After the solution was further stirred for 4 hours, the solvent was evaporated off. A white solid was precipitated, filtrated, washed with water, and then dried to afford compound **G8** (1.13 g, total yield 67.8 %) as a white solid. M.p.: 151-152°C. ^{1}H NMR (500 MHz, acetone-d_6): δ 8.64 (d, *J* = 2.4 Hz, 1H), 8.27 (d, *J* = 9.2 Hz, 1H), 8.23–8.07 (m, 3H), 7.78–7.71 (m, 2H), 4.03–3.99 (m, 9H). ^{13}C NMR (125 MHz, acetone-d_6): δ144.3, 133.0, 132.6, 130.9, 129.0, 128.5, 128.1, 127.7, 119.3, 117.4, 56.9. HRMS (ESI): *m/z* calcd for $[M\text{-}PF_6]^+$ $C_{13}H_{16}N^+$: 186.1342; found: 186.1340.

Synthesis of G9. To a mixture of 1-naphthalenemethylamine (628mg, 4 mmol) and potassium carbonate (2.8 g, 20 mmol) in CH_3CN (50 mL) was added MeI (2.28 g, 20 mmol), and the mixture was stirred under r.t. overnight. Then, the reaction mixture was filtered, and the filtrate was concentrated in vacuo. The residue was washed with ethyl ether several times. The chloride salt was dispersed in 30 mL acetone, which was then added saturated aqueous NH_4PF_6 solution until a clear solution was obtained. After the solution was further stirred for 4 hours, the solvent was evaporated off. A white solid was precipitated, filtrated, washed with water, and then dried to afford compound **G9** (1.23 g, total yield 89.1 %) as a white solid. M.p.: 141-144 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ 8.52 (d, *J* = 8.6 Hz, 1H), 8.18 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 7.1 Hz, 1H), 7.77–7.61 (m, 3H), 5.30 (s, 2H), 3.40 (s, 9H). ^{13}C NMR (125 MHz, acetone-d_6): δ 134.2, 133.8, 133.0, 131.9, 129.3,

127.6, 126.4, 125.2, 124.1, 123.6, 65.2, 65.2, 52.8, 52.8, 52.8, 29.4. HRMS (ESI): *m/z* calcd for $[M\text{-}PF_6]^+$ $C_{14}H_{18}N^+$: 200.1434; found: 200.1432.

X-Ray analysis: CCDC-1499509 (*rac*-**2**), 938490 (*rac*-**2·G2**), and 1498942 (*rac*-**2·G13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for *rac*-2: $C_{69}H_{54}O_6$, CCDC-1499509, M_w = 979.12, crystal size 0.34 x 0.28 x 0.05 mm^3, monoclinic, space group *P2*(1)/*n*, *a* = 20.925(4) Å, *b* = 12.251(2) Å, *c* = 25.897(5) Å, *α* = 90°, *β* = 105.59(3)°, *γ* = 90°, *V* = 6395(2) Å^3, *Z* = 4, *Dc* = 1.017 Mg m^{-3}, *T* = 173(2) K, *μ* = 0.064 mm^{-1}, 27583 reflections measured, 11223 unique (R_{int} = 0. 0842), final *R* indices [*I*2σ(*I*)]: R_1 = 0. 0717, wR_2 = 0.1947, *R* indices (all data): *R*1 = 0. 0993, wR_2 = 0.2145.

Crystal data for *rac*-2·G2: $C_{76}H_{70}F_6NO_7PS$, CCDC-938490, M_w = 1286.36, crystal size 0.48 x 0.14 x 0.12 mm^3, monoclinic, space group *C2*/*c*, *a* = 42.204(8) Å, *b* = 14.938(3) Å, *c* = 25.555(5) Å, *α* = 90°, *β* = 104.490(3)°, *γ* = 90°, *V* = 15599(5) Å^3, *Z* = 8, *Dc* = 1.096 Mg m^{-3}, *T* = 173(2) K, *μ* = 0. 124 mm^{-1}, 48606 reflections measured, 13716 unique (R_{int} = 0.0612]), final *R* indices [*I*2σ(*I*)]: R_1 = 0.1201, wR_2 = 0.3089, *R* indices (all data): *R*1 = 0.1421, wR_2 = 0.3213.

Crystal data for *rac*-2·G13: $C_{78}H_{68}F_6NO_6P$, CCDC-1498942, M_w = 1260.3, crystal size 0.53 x 0.30 x 0.30 mm^3, monoclinic, space group *C2*/*c*, *a* = 42.201(8) Å, *b* = 15.139(3) Å, *c* = 25.498(5) Å, *α* = 90°, *β* = 104.65(3)°, *γ* = 90°, *V* = 15761(5) Å^3, *Z* = 8, *Dc* = 1.062 Mg m^{-3}, *T* = 173(2) K, *μ* = 0.095 mm^{-1}, 45760 reflections measured, 13831 unique (R_{int} = 0.0902), final *R* indices [*I*2σ(*I*)]: R_1 = 0. 1556, wR_2 = 0.3721, *R* indices (all data): *R*1 = 0.1980, wR_2 = 0.3902.

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Keywords: host-guest chemistry • complexation • macrocyclic arene • quaternary ammonium salts • *N*-heterocyclic salts

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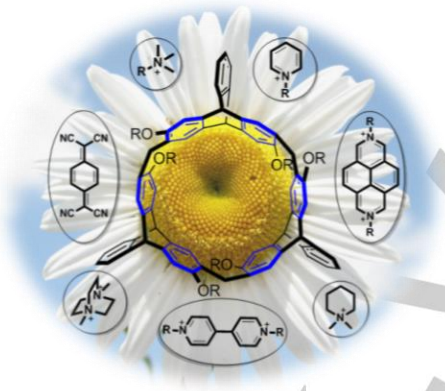
Racemic 2,6-helic[6]arene and its hexamethyl-substituted derivative showed high affinities towards a wide scope of tested organic guests including quaternary ammonium salts, *N*-heterocyclic salts and tetracyanoquinodimethane. The complexation between the hosts and the guests were investigated by NMR spectra, X-ray crystal structures and theoretical calculation.



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Complexation of Racemic 2,6-Helic[6]arene and Its Hexamethyl-Substituted Derivative with Quaternary Ammonium Salts, N-Heterocyclic Salts and Tetracyanoquinodimethane