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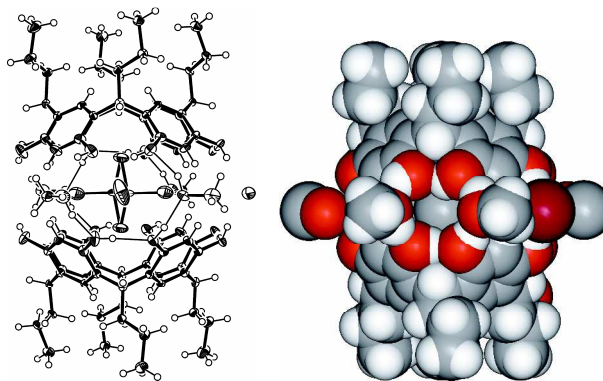
Encapsulation of Tetramethyl Phosphonium Cations

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Keywords:	Supramolecular Chemistry, Resorcinarenes, Capsules, X-ray crystallography, Mass spectrometry

Encapsulation of Tetramethyl Phosphonium Cations

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The tetramethylphosphonium cation is encapsulated into the cavity of an eclipsed 1:2 dimeric capsule formed by two resorcinarene or pyrogallarene molecules. In solution and in gas phase pyrogallarene was found to be far more stable 1:1 open and 1:2 dimeric capsular complexes than resorcinarene.



Encapsulation of Tetramethyl Phosphonium Cations

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The weak interactions and capsule formation of tetramethylphosphonium (TMP) cation with resorcinarenes **1** and **2** and the corresponding pyrogallarenes **3** and **4** were studied in the solid state by single crystal X-ray diffraction, in solution by NMR and in the gas phase by mass spectrometry. In methanol-D₄, the NMR titration studies reveal that the association constants for the 1:1 complexes of TMP@**3** and TMP@**4** are much higher (TMP@**4**:390±37 M⁻¹) than for the corresponding TMP@**1** and TMP@**2** (TMP@**2**:130±10 M⁻¹) complexes. In the gas phase both monomeric 1:1 TMP@**1**-TMP@**4** complexes as well as the dimeric 1:2 capsule complexes, TMP@**1**₂-TMP@**4**₂ were observed. The 1:1:2 molar mixtures of **1**:**2**:TMP or **3**:**4**:TMP resulted in homo- and heterocapsules TMP@**1**₂, TMP@**1**+**2** and TMP@**2**₂ with the expected statistical 1:2:1 ratio. Using 1:1:2 ratio of **1**:**3**:TMP, **1**:**4**:TMP, **2**:**3**:TMP or **2**:**4**:TMP showed a marked preference to the homopyrogallarene capsules TMP@**3**₂ and TMP@**4**₂ thus supporting the stronger complexation of TMP with **3** and **4** as observed in solution. The X-ray structures[†] confirmed the dimeric capsular structures with only minor structural differences to the corresponding tetramethylammonium (TMA) capsules reported earlier.

Keywords: Supramolecular Chemistry, Resorcinarenes, Capsules, X-ray crystallography, Mass spectrometry

INTRODUCTION

For many years, self-assembling, reversibly hydrogen-bonded capsules [1] have contributed a great deal to our current understanding of enzyme action. Considerable interest has been focused on the design and synthesis of biomimetic receptors. In order to achieve convergent arrangement of binding sites, many of these receptors have utilized the cone shape of the resorcinarenes and pyrogallarenes for a variety of applications [2]. The easy large scale

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[†] Crystallographic data for structures **5**⁺@**1**₂·Br⁻·16H₂O and **5**⁺@**2**₂·Br⁻·4MeOH have been deposited with the Cambridge Crystallographic Data Centre as CCDC 687169 and 687170. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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3 preparations of these compounds makes them very attractive building blocks in
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5 supramolecular chemistry [3].
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8 Resorcinarenes and pyrogallarenes have the ability to easily form molecular capsules via
9 hydrogen bonded networks. Open inclusion complexes [4], dimers [5], hexamers [3a, 6],
10 larger supramolecular [2b] and tubular [2b, 7] assemblies linked together by hydrogen
11 bonding with cavities aimed at trapping cationic [4b, 5] and neutral [2c, 8] guests. Recently
12 anion complexation using resorcinarene based cavitand has been reported [9]. Ammonium
13 cations have proven to be good guest candidates for resorcinarene complexation since they
14 have the possibility to interact *via* cation $\cdots\pi$ and C-H $\cdots\pi$ interactions as well as
15 advantageously fill the empty space in the hollow cavity of the resorcinarene host [5]. Under
16 neutral conditions, closer to the biological environment, the binding of quaternary alkyl
17 ammonium cations is significantly weakened compared to complexation in alkaline solvents
18 [10]. Mass spectrometry [11] is an important tool to examine binding interactions of cations
19 in the gas phase. It has the advantage of proving the complexation without solvent
20 interference. Dimeric [5a] and hexameric [6d] capsules of resorcinarenes, pyrogallarenes and
21 related compounds encapsulating small and large cations have been shown to prevail in the
22 gas phase [12] without solvent mediation and have been predicted to be directly hydrogen
23 bonded.
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27 Our aim was to probe other cationic species which could act in a similar way as the
28 tetraalkylammonium cations extensively studied by us [5a-5g]. Previously Rebek *et al.* [13]
29 showed the complexation of tetramethylphosphonium cation by resorcinarenes and
30 pyrogallarenes in solution. The longer P-C bond length compared to the C-N bond increases
31 the volume of the tetramethyl phosphonium (TMP) cation to 115 Å³ from the 105 Å³ of that of
32 tetramethyl ammonium (TMA) cation. The softer nature of the phosphorous atom and the
33 slightly larger size could lead to different complexation behavior with resorcinarenes and
34 pyrogallarenes. Thus we report herein examples of the complexation and capsule formation
35 of tetramethylphosphonium (TMP) cation with core resorcinarenes and pyrogallarenes in the
36 solid state supplemented by complexation studies in solution by NMR and in the gas phase by
37 MS. In the gas phase, competition studies reveals the formation of heterodimers and showed
38 that the complexation/encapsulation of TMP with pyrogallarenes is markedly more efficient
39 than with resorcinarenes.
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RESULTS AND DISCUSSION

X-RAY STRUCTURES

The solid state complexation and encapsulation properties of the alkyl resorcinarenes **1** and **2** as well as pyrogallarenes **3** and **4** with tetramethyl phosphonium cation **5** (Figure 1) were investigated in crystallization studies from aqueous methanol solution using a 1:2 guest to host molar ratio. We were able to obtain capsules for single crystal X-ray determination from resorcinarenes **1** and **2** with tetramethyl phosphonium bromide **5b**. All solid state complexation experiments with pyrogallarenes **3** and **4** or with the tetramethyl phosphonium chloride **5a** resulted in a microcrystalline powder precipitate.

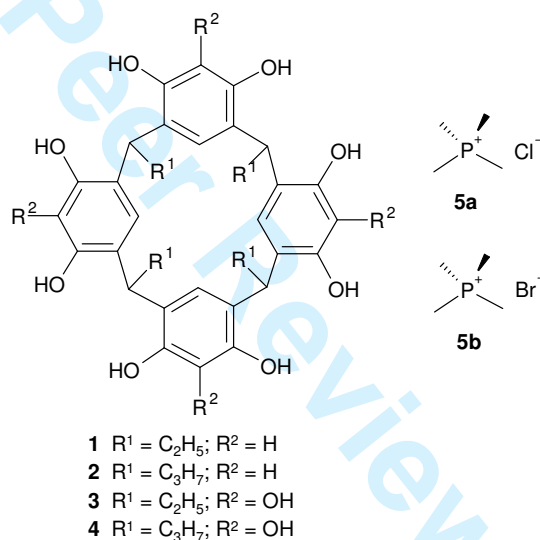


Figure 1: Hosts **1 - 4** and cationic guests **5a** and **5b**

In the capsule, $5^+@1_2 \cdot Br^- \cdot 16H_2O$, two molecules of **1** are linked via water molecules and, as expected, the cation 5^+ is encapsulated inside the cavity formed by the two resorcinarene hosts (Figure 2). However, the disorder of the TMP is so severe, that definite conclusions about its orientation and possible interactions with the host could not be made. As with other C2 resorcinarene capsules [5d] the bromide anion is found to reside in the small pocket between the ethyl groups of the host via weak C-H \cdots anion interactions. The encapsulation of the spherical cation and the location of the anion is very similar to that observed by us within the eclipsed TMA@ $1_2 \cdot Br^- \cdot 8MeOH$ [5d] capsule complex. The dimensions of the corresponding

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TMA capsule are very similar to the TMP capsule reported here. Table 1 lists the values of the capsular dimensions for four TMP and TMA capsules.

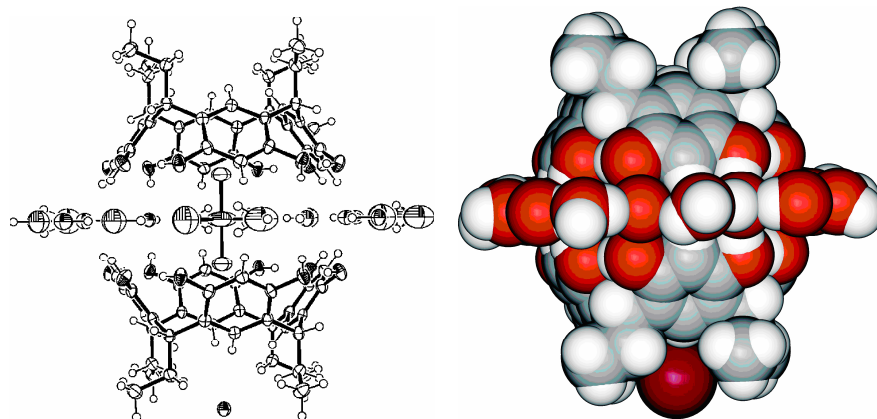


Figure 2: Ortep and CPK plots of the X-ray structure of hydrogen bonded solvent-anion mediated resorcinarene capsule $5^+@1_2 \cdot \text{Br}^- \cdot 16\text{H}_2\text{O}$.

As in $5^+@1_2 \cdot \text{Br}^- \cdot 16\text{H}_2\text{O}$ the methanol molecules in the capsule $5^+@2_2 \cdot \text{Br}^- \cdot 4\text{MeOH}$ mediated the capsule formation (Figure 3). The encapsulated TMP cation inside the cavity is also severely disordered. In addition to solvent molecules, the capsule is also mediated by Br⁻ anions. This is similar to the eclipsed $\text{TMA}@2_2 \cdot \text{Cl}^- \cdot 4\text{MeOH}$, $\text{TMA}@2_2 \cdot \text{Cl}^- \cdot 4\text{EtOH}$ and $\text{TMA}@2_2 \cdot \text{Br}^- \cdot 4\text{EtOH}$ capsules reported earlier by us.^{5d} The capsule $5^+@2_2 \cdot \text{Br}^- \cdot 4\text{MeOH}$ resembles more the previously reported ethanol mediated capsules having similar crystallographic parameters (space group, cell dimensions etc.) than the C₂ resorcinarene TMP capsule $5^+@1_2 \cdot \text{Br}^- \cdot 16\text{H}_2\text{O}$ shown in Figure 2. The distance between resorcinarene moieties in $5^+@2_2 \cdot \text{Br}^- \cdot 4\text{MeOH}$ is also slightly longer (0.25 – 0.51 Å) when compared to the mentioned TMA capsules, but otherwise the capsule dimensions are similar (Table 1). Due to the different location of the bromine anions within the capsules, the ion pair (TMP⁺ and Br⁻) is slightly more separated in the C₂ than in the C₃ capsule (Table 1).

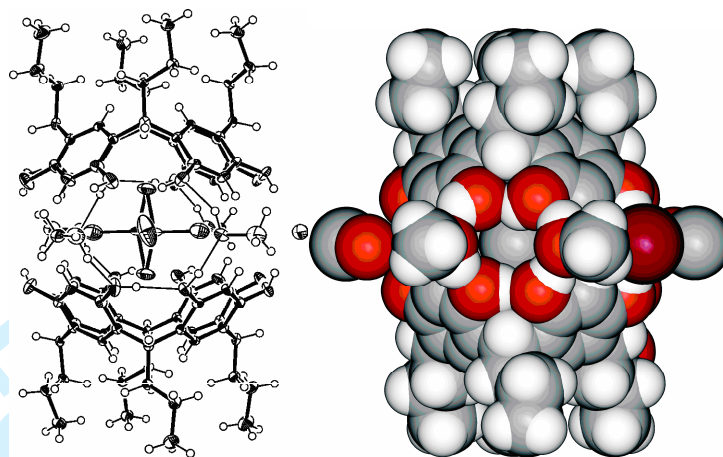


Figure 3: Ortep and CPK plots of the X-ray structure of hydrogen bonded solvent-anion mediated resorcinarene **2** capsule $5^+@2_2 \cdot Br^- \cdot 4MeOH$.

NMR AND MASS SPECTROMETRIC STUDIES

Significant complexation induced upfield shifts of the guest signals were observed when resorcinarene **2** and pyrogallarene **4** were mixed with **5a** or **5b** in methanol- D_4 similar to what rebek *et al* [13] reported. The titration data clearly supports a fast guest exchange compared to the NMR timescale at 303 K with a 1:1 complexation model in methanol- D_4 determined by Job plot [14] experiments. The efficiency with which the solvent competes with the hydrogen-bonding system of the host, how it competes with the TMP cation in the inclusion to the host cavity and the fact that methanol very efficiently solvates the ion pair explains well why the possible 1:2 dimeric capsule complex is not formed in dilute solutions at 303 K. The association constants for 5^+ at 303K for hosts **2** and **4** were determined to be 130 ± 10 and $390 \pm 37 M^{-1}$, respectively, by the non-linear least-squares fitting of the titration curve [15]. The association constants of the pyrogallarene were much higher than with the respective resorcinarene as expected due to the more π -basic character of the pyrogallarenes.

Table 1: The dimension for TMP and TMA [5d] capsules.

Capsule	TMP@1 ₂ ·Br ⁻ ·16H ₂ O	TMA@1 ₂ ·Br ⁻ ·8MeOH	TMP@2 ₂ Br ⁻ ·4MeOH	TMA@2 ₂ ·Br ⁻ ·4EtOH
Capsule mediating hydrogen bonds to solvents/Å	2.68-2.72	2.67-2.69	2.68-2.96	2.66-2.75
Capsule mediating hydrogen bonds to Br ⁻ /Å	-	-	3.15	3.23,3.25
Distance between the capsule halves/Å ^a	9.00	8.86	8.85	8.59
Distance between the centroids of opposite aromatic rings of a resorcinarene molecule/Å	6.85	6.87	6.84/6.94	6.79/6.97
Capsule conformation	eclipsed	eclipsed	eclipsed	eclipsed
Closest P/N...Br distance/Å	7.69	7.76	6.47	7.07

^a Defined as a distance between the planes formed by the methine bridges of the resorcinarenes.

Mass spectrometric studies of complexes of resorcinarenes with singly charged alkyl ammonium cations showed that the dimeric molecular capsules of resorcinarene also exist in the gas phase [5d, 5f]. For electrospray ionization, solution of **5a** and **5b** with the corresponding resorcinarenes and pyrogallarenes were used. The base peaks corresponding to the open monomeric inclusion complexes of resorcinarene [**5@1**]⁺ (*m/z* 691), [**5@2**]⁺ (*m/z* 747) and pyrogallarenes [**5@3**]⁺ (*m/z* 755), [**5@4**]⁺ (*m/z* 811) were easily detected. Without solvent interference in the ion source of the instrument, dimeric capsules containing the TMP guests as [**5@1**₂]⁺ (*m/z* 1291), [**5@2**₂]⁺ (*m/z* 1403) for the resorcinarenes and [**5@3**₂]⁺ (*m/z* 1419), [**5@4**₂]⁺ (*m/z* 1531) for the pyrogallarenes were also observed. This is in line with earlier results using tetraalkylated ammonium cations [5] and tetramethylphosphonium cation [13].

Upon mixing a 1:1 molar solution of **1** and **2**, heterodimers are quickly formed with **5**⁺ as the guest. Figure 4 depicts the region of the spectra in which the charged dimeric complexes [**5@1**₂]⁺ (*m/z* 691) and [**5@2**₂]⁺ (*m/z* 1291) appears. The spectra (a) and (b) correspond to the two solutions before mixing and (c) correspond to the two solutions after mixing. In (c), the

two homodimers and the heterodimer $5^+@1+2$ are formed with intensity distribution close to the statistically 1:2:1 ratio as expected. This is also similar when pyrogallarenes **3** and **4** are mixed in a 1:1 ratio (S6, Supplementary material).

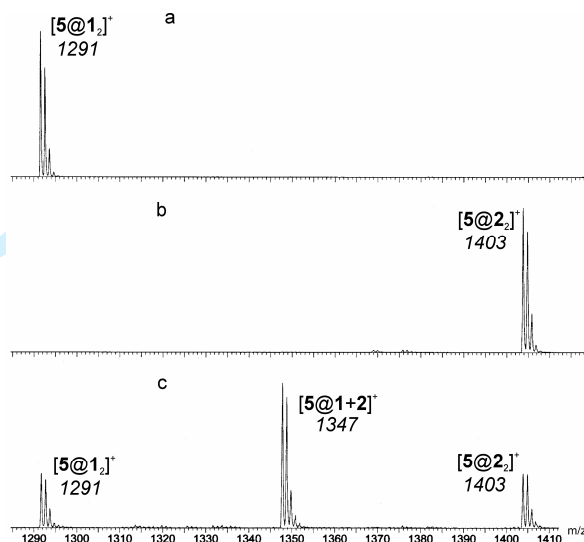


Figure 4: Partial ESI mass spectra of: a) $5^+@1_2$, b) $5^+@2_2$ and c) 5^+ with a 1:1 mixture of **1** and **2** in methanol. Heterodimer formation is clearly observed in the statistical 1:2:1 ratio.

The difference in the complexation strength is evident when resorcinarene **1** or **2** is mixed together with pyrogallarene **3** or **4**, respectively, in the presence of **5a** or **5b**. The pyrogallarene homodimers $5^+@3_2$ and $5^+@4_2$ are markedly more favoured than the resorcinarene homodimers $5^+@1_2$ and $5^+@2_2$ or the heterodimers $5^+@1+4$ and $5^+@2+4$ (Figure 5). The biased equilibrium reflecting the difference in the stabilities of the 1:1 complexes is reached before the first MS spectrum can be recorded (ca. 30 s after mixing the two solutions of the resorcinarene and pyrogallarene complexes).

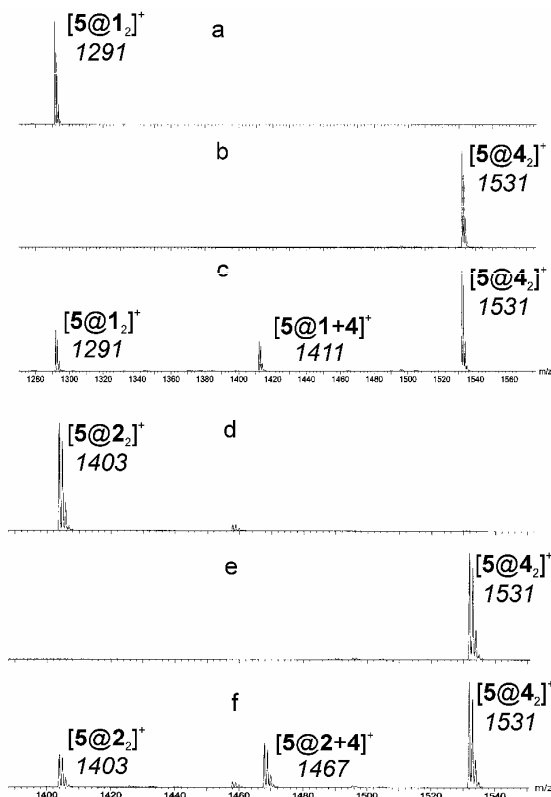


Figure 5: Partial ESI mass spectra of: (a) $5^+@1_2$, (b) $5^+@4_2$ and (c) 5^+ with a 1:1 mixture of **1** and **4**, (d) $5^+@2_2$, (e) $5^+@4_2$ and (f) 5^+ with a 1:1 mixture of **2** and **4**. Heterodimer formation is clearly observed and it is seen that the dimer formation with pure pyrogallarene is more favoured.

CONCLUSION

In conclusion, we have demonstrated that the complexation of tetramethylphosphonium cation with resorcinarenes and pyrogallarenes behaves very similarly as the corresponding tetramethylammonium cation. The structural studies in the solid state, in solution and in the gas phase confirm the structures of the 1:1 open complexes in solution and gas phase and 1:2 dimeric capsules in solid state and in gas phase. The complexation studies with NMR in methanol- D_4 revealed ca. three times more stable 1:1 complexes with pyrogallarenes as compared to corresponding resorcinarenes. The complexes in solution are all 1:1 at 303 K due to the fast exchange of the complexed guest and free guest at NMR timescale. The 1:1 complex is the prerequisite for the capsule formation observed in the solid state and in the gas phase. Experiments aiming at the formation of heterodimers from two different homodimers in the gas phase clearly show the monomer exchange to be fast on the human timescale. It was also seen in the gas phase that the complexations with pyrogallarenes are more favoured.

GENERAL REMARKS

The resorcinarenes and pyrogallarenes were synthesized according to reported procedures [16]. The tetramethylphosphonium salts were commercially available.

NMR TITRATION

^1H NMR titrations were performed in methanol- D_4 by titrating 0.5 ml of a 0.002M solution of the tetramethylphosphonium chloride or bromide salt with a 0.02M solution of the resorcinarene or pyrogallarene. The ^1H NMR spectra of each titration step was measured on a 500 MHz Bruker Avance DRX spectrometer. Binding constants were obtained by the non-linear least-squares fitting of the titration curve.

ESI-TOF MASS SPECTROSCOPY

The mass spectrometric experiments were performed with a Micromass LCT ESI-TOF instrument equipped with a Z geometry electrospray ion source. For positive ion spectra, the samples were introduced into the source as methanol solution mixtures of **1** (0.5 mM) and the salts of charged cations 5^+ (0.5 mM) at flow rates of $30 \mu\text{l min}^{-1}$. Constant spray and highest intensities were achieved with a capillary voltage of 3885 V at a source temperature of 80°C and a dissolution temperature of 120°C . Other selected source parameters were as follows: sample cone voltage 40–60 V; extraction cone voltage 5–6 V; flow of cone gas 10 l h^{-1} ; flow of dissolution gas 150 l h^{-1} . Other parameters did not influence much the ion intensities. For the examination of heterodimer formation, two of the sample solutions were mixed in a 1:1 molar ratio and then subjected to the same experiments. Multiple scans (50–200) were recorded and averaged for each spectrum in order to improve the signal-to-noise ratio.

CRYSTAL STRUCTURES

Suitable single crystals for X-ray analysis were obtained from slow evaporation of resorcinarenes **1** or **2** and TMP bromide **5b** in water/methanol mixture. The X-ray crystallographic data for complexes were collected with Bruker-Nonius Kappa APEX-II diffractometer at $123.0 \pm 0.1 \text{ K}$ using graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). COLLECT [17] data collection software was utilized and data was processed with DENZO-SMN [18]. The structures were solved by direct methods, using SIR-2002 [19], and refined on F^2 , using SHELXL-97 [20]. The reflections were corrected for Lorentz polarization

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3 effects but absorption correction was not applied. Geometrical restraints (DFIX, DANG)
4 were used to fix O-H distances and H-O-H angles in the refinement. The figures were drawn
5 with ORTEP-3 for Windows [21] and MERCURY [22]. The crystal data and other
6 parameters are presented in Table 2.
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11 The cation 5^+ in both structures is severely disordered and the determination of exact
12 orientation of the cation inside the capsule was not possible. The hydrogen atoms were not
13 determined for the cation. In $5^+@1_2 \cdot Br^- \cdot 16H_2O$ some water molecules are disordered over two
14 sites. In $5^+@2_2 \cdot Br^- \cdot 4MeOH$ methanol molecules are also disordered. Half of the methanol
15 molecules have two different orientations and the less occupied oxygen position was treated
16 isotropically. Hydrogens located for water molecules and methanol hydroxyls were fixed to
17 distances of 0.975 Å from oxygens with isotropic temperature factors (1.2 or 1.5 times the O
18 temperature factor). All hydrogens for water and methanol molecules could not be
19 determined. The other hydrogen atoms were calculated to their idealized positions with
20 isotropic temperature factors (1.2 or 1.5 times the parent atom temperature factor) and refined
21 as riding atoms.
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Table 2: Crystal data and structure refinement parameters

Capsule	$5^+ @ 1_2 \cdot \text{Br}^- \cdot 16\text{H}_2\text{O}$	$5^+ @ 2_2 \cdot \text{Br}^- \cdot 4\text{MeOH}$
Empirical formula	$\text{C}_{75}\text{H}_{96}\text{BrO}_{32}\text{P}$	$\text{C}_{27}\text{H}_{47}\text{NO}_4$
Formula weight	1620.40	449.66
Crystal system	Tetragonal	Triclinic
Space group	I4/m	<i>P</i> -1
<i>a</i> (Å), α (°)	14.2933(5), 90	13.2134(3), 105.766(1)
<i>b</i> (Å), β (°)	14.2933(5), 90	13.4323(2), 90.667(1)
<i>c</i> (Å), γ (°)	21.1417(8), 90	14.6404(3), 118.526(1)
Volume (Å ³)	4319.2(3)	2166.11(7)
<i>Z</i>	2	1
Density _{calc} (Mg/m ³)	1.246	1.218
Abs. coefficient (mm ⁻¹)	0.573	0.560
<i>F</i> (000)	1704	844
θ range (°)	3.22 - 25.01	2.49 - 25.00
Index ranges	$-16 \leq h \leq 16, -16 \leq k \leq 16$ $-22 \leq l \leq 25$	$-15 \leq h \leq 15, -15 \leq k \leq 15$ $-17 \leq l \leq 17$
Reflections collected	13356	13432
<i>R</i> _{int}	0.0841	0.0331
Data/restraints/parameters	1954 / 8 / 152	7603 / 2 / 530
Goodness-of-fit on <i>F</i> ²	1.061	1.034
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ =0.0728, <i>wR</i> ₂ =0.1870	<i>R</i> ₁ =0.1031, <i>wR</i> ₂ =0.2947
<i>R</i> indices (all data)	<i>R</i> ₁ =0.0980, <i>wR</i> ₂ =0.2069	<i>R</i> ₁ =0.1273, <i>wR</i> ₂ =0.3180
Largest diff. peak and hole (eÅ ⁻³)	0.73 and -0.53	0.84 and -2.71 ^a

^a close to Br1

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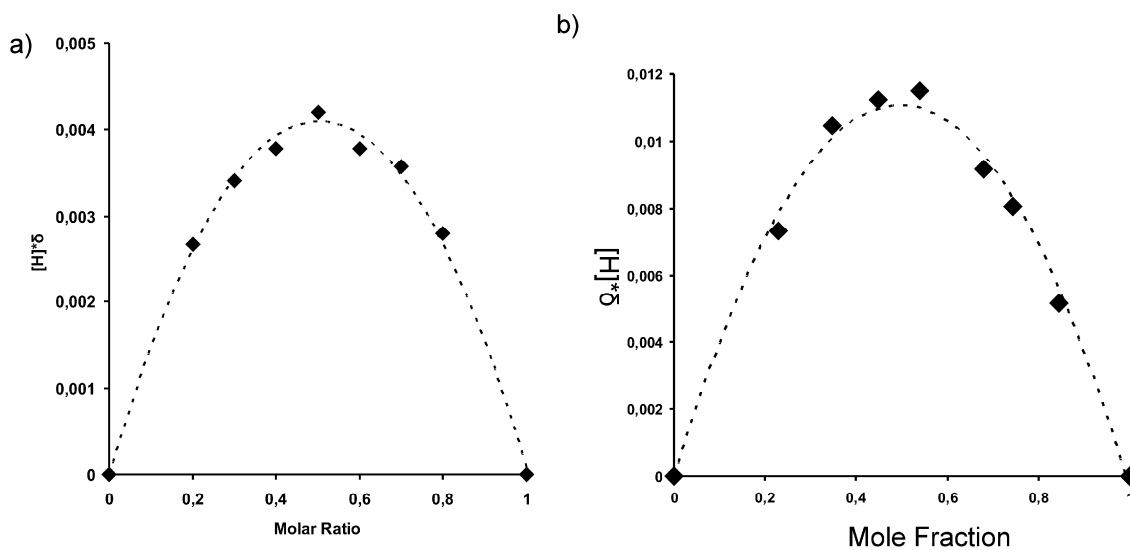
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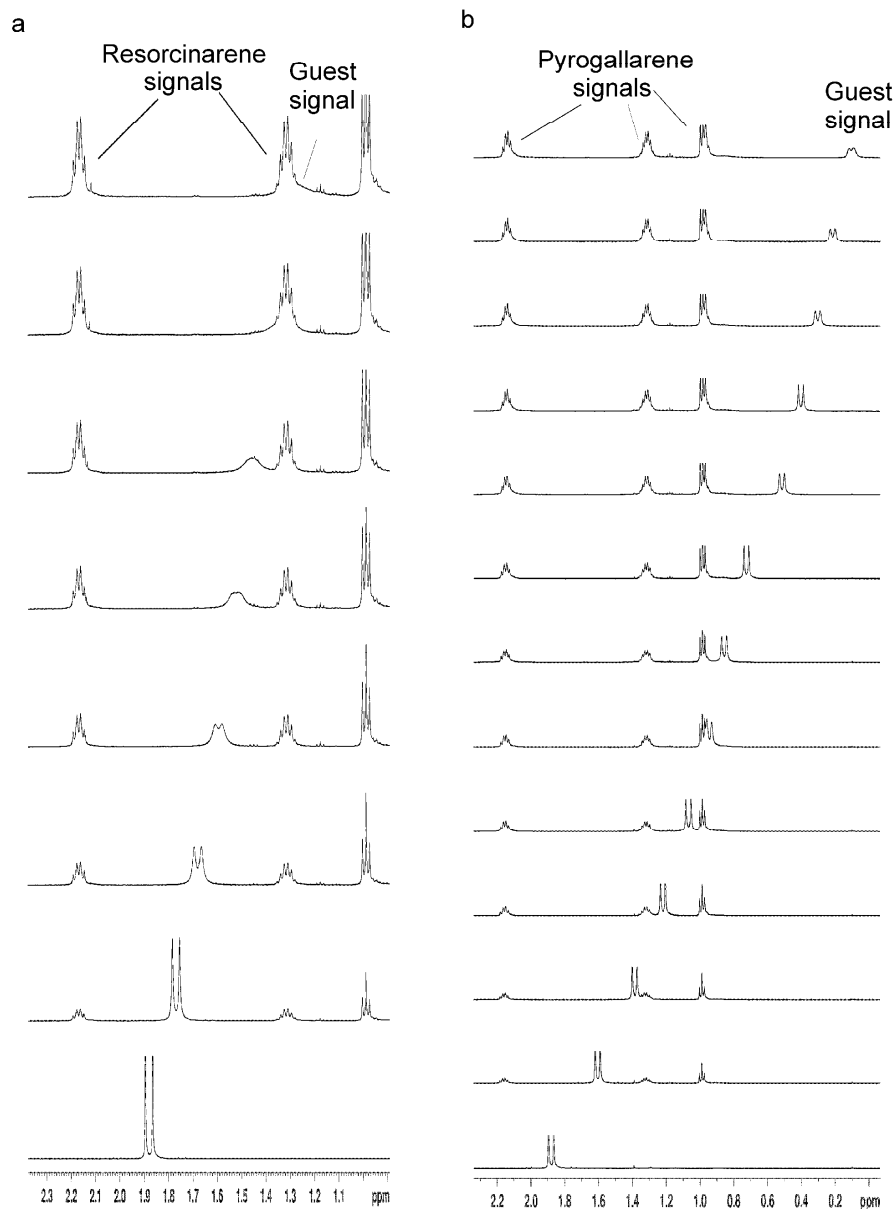
Encapsulation of Tetramethyl Phosphonium Cations

Ngong Kodiah Beyeh, Arto Valkonen and Kari Rissanen*

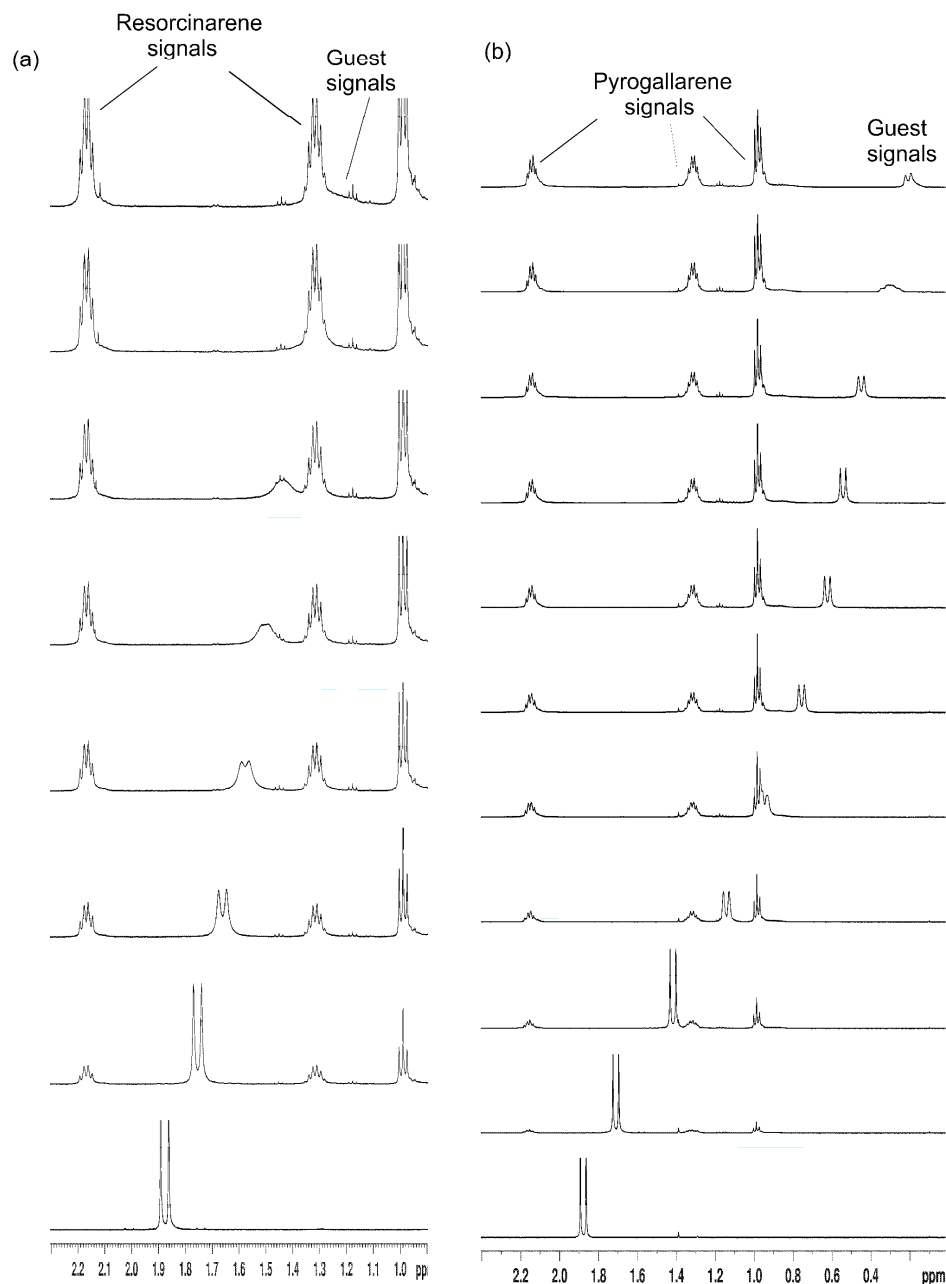
Supporting Material



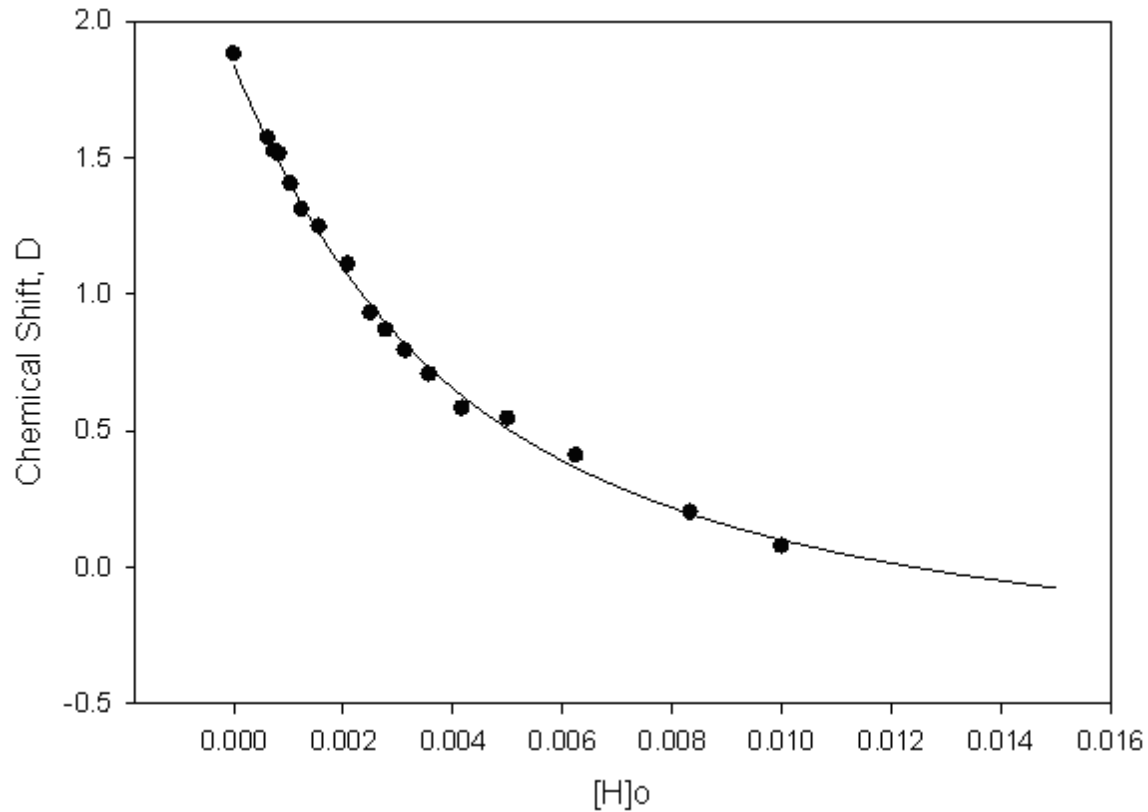
S1: Job plot of the complexation of: a) 5^+Br^- by **2** and b) 5^+Br^- by **4** as an example of a 1:1 complex stoichiometry at 303 K.



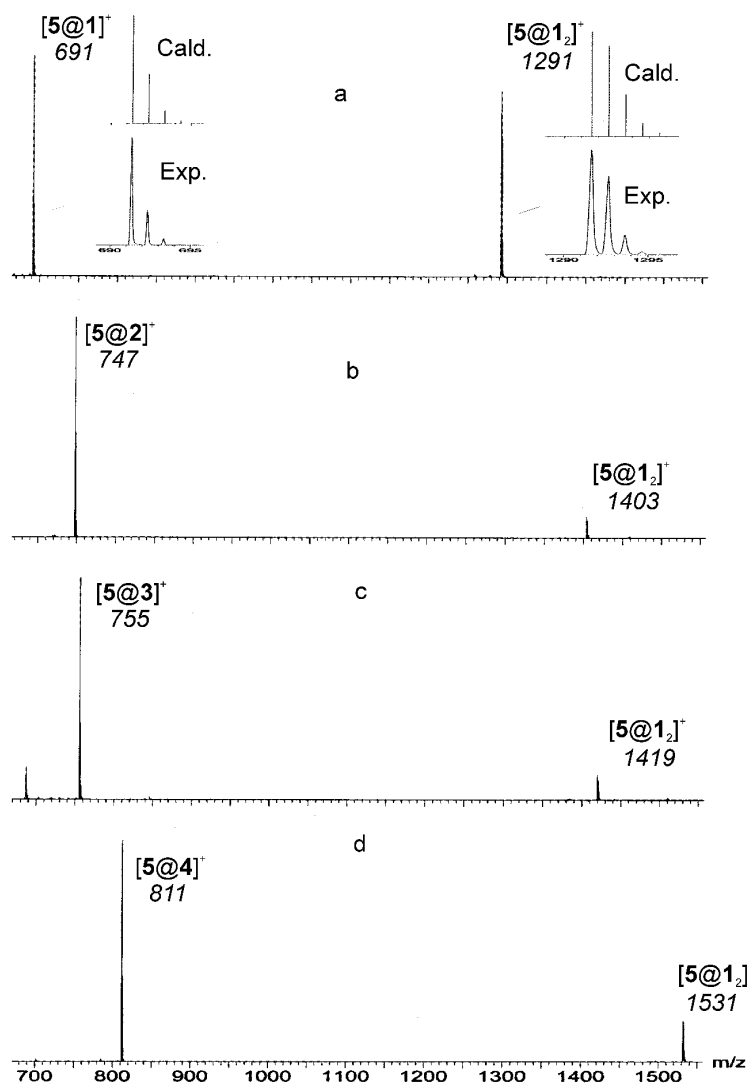
S2: ¹H NMR titration of (a) resorcinarene **2** with 5⁺Br⁻ with addition of 0.4, 0.8, 1.2, 1.6, 2.0, 2.8, 3.6 equiv. and (b) pyrogallarene **4** with 5⁺Br⁻ with addition of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.4, 3.0 equiv. in methanol-D₄ at 303 K. A solution of 0.02M of the host was titrated to a 0.002 M solution of the guest.



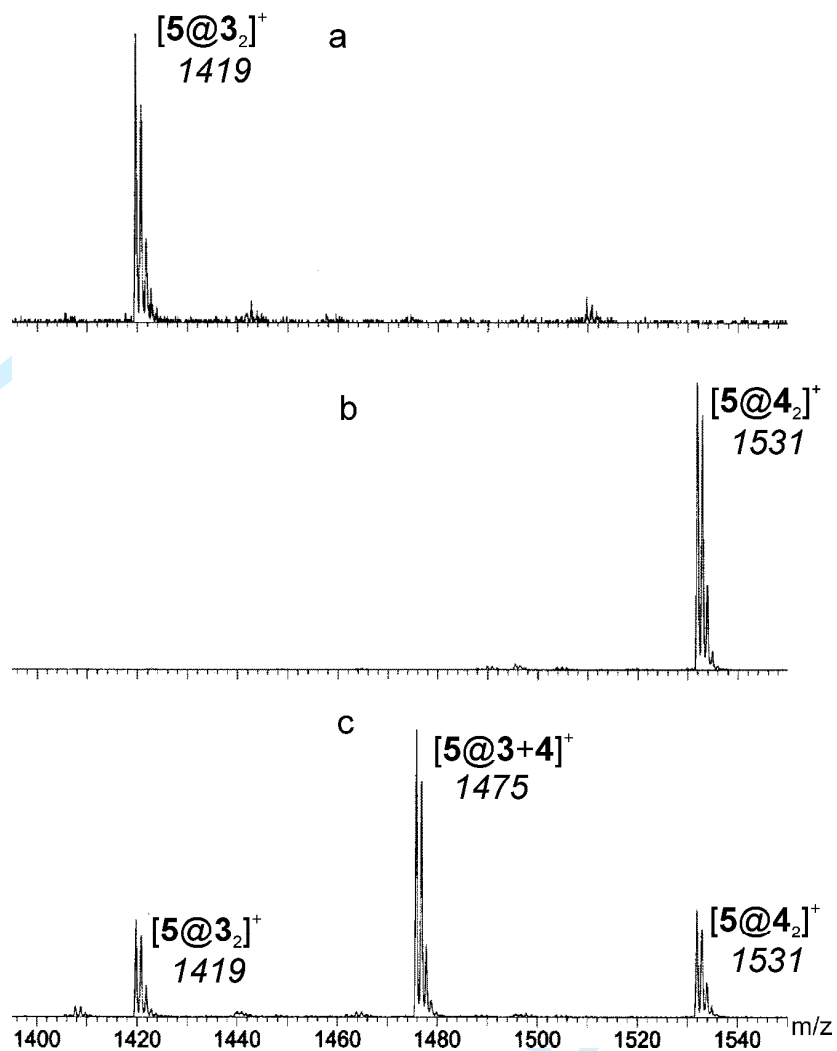
S3: ^1H NMR titration of (a) resorcinarene **2** with 5^+Cl^- with addition of 0.4, 0.8, 1.2, 1.6, 2.0, 2.8, 3.6 equiv. and (b) pyrogallarene **4** with 5^+Cl^- with addition of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.6, 2.0, 2.4, 3.0 equiv. in methanol- d_4 at 303 K. A solution of 0.005M of the host was added to a 0.02 M solution of the guest.



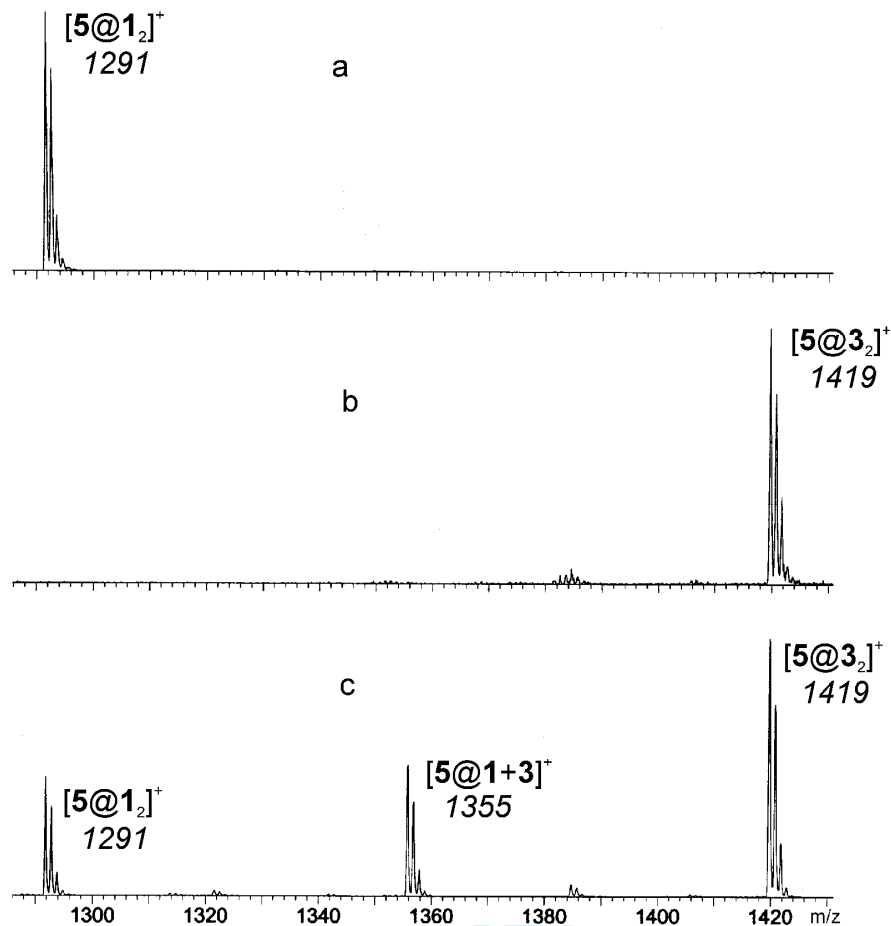
S4: ¹H NMR titration of TMP **5b** with Pyrogallarene **4** in Methanol-D₄. Points are experimental and curve is calculated.



S5: Positive ion ESI mass spectra of a mixture in methanol of a) 5⁺Br⁻ and **1**, b) 5⁺Br⁻ and **2**, c) 5⁺Br⁻ and **3** and d) 5⁺Br⁻ and **4**. The insets in (a) show the calculated and experimental isotope patterns of the [5@1]⁺ and [5@1₂]⁺.



S6: Partial ESI mass spectra of: a) $5^+@3_2$, b) $5^+@4_2$ and c) 5^+ with a 1:1 mixture of **3** and **4** in methanol. Heterodimer formation is clearly observed in the statistical 1:2:1 ratio.



S7: Partial ESI mass spectra of: a) $5^+@1_2$, b) $5^+@3_2$ and c) 5^+ with a 1:1 mixture of **1** and **3** in methanol. Heterodimer formation is clearly observed and it is seen that the dimer formation with pure pyrogallarene is more favored.

Table 1: The dimension for TMP and TMA [5d] capsules.

Capsule	TMP@1 ₂ ·Br ⁻ ·16H ₂ O	TMA@1 ₂ ·Br ⁻ ·8MeOH	TMP@2 ₂ ·Br ⁻ ·4MeOH	TMA@2 ₂ ·Br ⁻ ·4EtOH
Capsule mediating hydrogen bonds to solvents/Å	2.68-2.72	2.67-2.69	2.68-2.96	2.66-2.75
Capsule mediating hydrogen bonds to Br ⁻ /Å	-	-	3.15	3.23,3.25
Distance between the capsule halves/Å ^a	9.00	8.86	8.85	8.59
Distance between the centroids of opposite aromatic rings of a resorcinarene molecule/Å	6.85	6.87	6.84/6.94	6.79/6.97
Capsule conformation	eclipsed	eclipsed	eclipsed	eclipsed
Closest P/N...Br distance/Å	7.69	7.76	6.47	7.07

^a Defined as a distance between the planes formed by the methine bridges of the resorcinarenes.

Table 2: Crystal data and structure refinement parameters

Capsule	$5^+ @ 1_2 \cdot Br^- \cdot 16H_2O$	$5^+ @ 2_2 \cdot Br^- \cdot 4MeOH$
Empirical formula	$C_{75}H_{96}BrO_{32}P$	$C_{27}H_{47}NO_4$
Formula weight	1620.40	449.66
Crystal system	Tetragonal	Triclinic
Space group	I4/m	<i>P</i> -1
a (Å), α (°)	14.2933(5), 90	13.2134(3), 105.766(1)
b (Å), β (°)	14.2933(5), 90	13.4323(2), 90.667(1)
c (Å), γ (°)	21.1417(8), 90	14.6404(3), 118.526(1)
Volume (Å ³)	4319.2(3)	2166.11(7)
Z	2	1
Density _{calc} (Mg/m ³)	1.246	1.218
Abs. coefficient (mm ⁻¹)	0.573	0.560
<i>F</i> (000)	1704	844
θ range (°)	3.22 - 25.01	2.49 - 25.00
Index ranges	$-16 \leq h \leq 16$, $-16 \leq k \leq 16$ $-22 \leq l \leq 25$	$-15 \leq h \leq 15$, $-15 \leq k \leq 15$ $-17 \leq l \leq 17$
Reflections collected	13356	13432
<i>R</i> _{int}	0.0841	0.0331
Data/restraints/parameters	1954 / 8 / 152	7603 / 2 / 530
Goodness-of-fit on <i>F</i> ²	1.061	1.034
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ =0.0728, w <i>R</i> ₂ =0.1870	<i>R</i> ₁ =0.1031, w <i>R</i> ₂ =0.2947
<i>R</i> indices (all data)	<i>R</i> ₁ =0.0980, w <i>R</i> ₂ =0.2069	<i>R</i> ₁ =0.1273, w <i>R</i> ₂ =0.3180
Largest diffr. peak and hole (eÅ ⁻³)	0.73 and -0.53	0.84 and -2.71 ^a

^a close to Br1

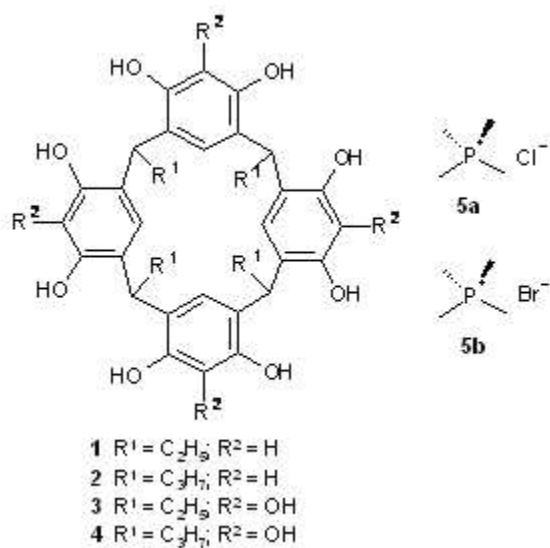


figure 1

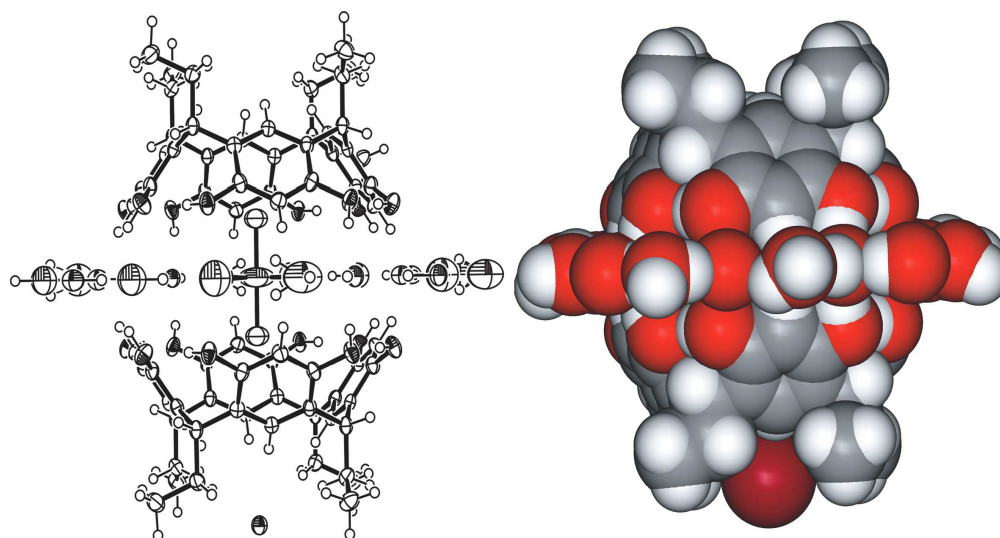


figure 2
199x106mm (300 x 300 DPI)

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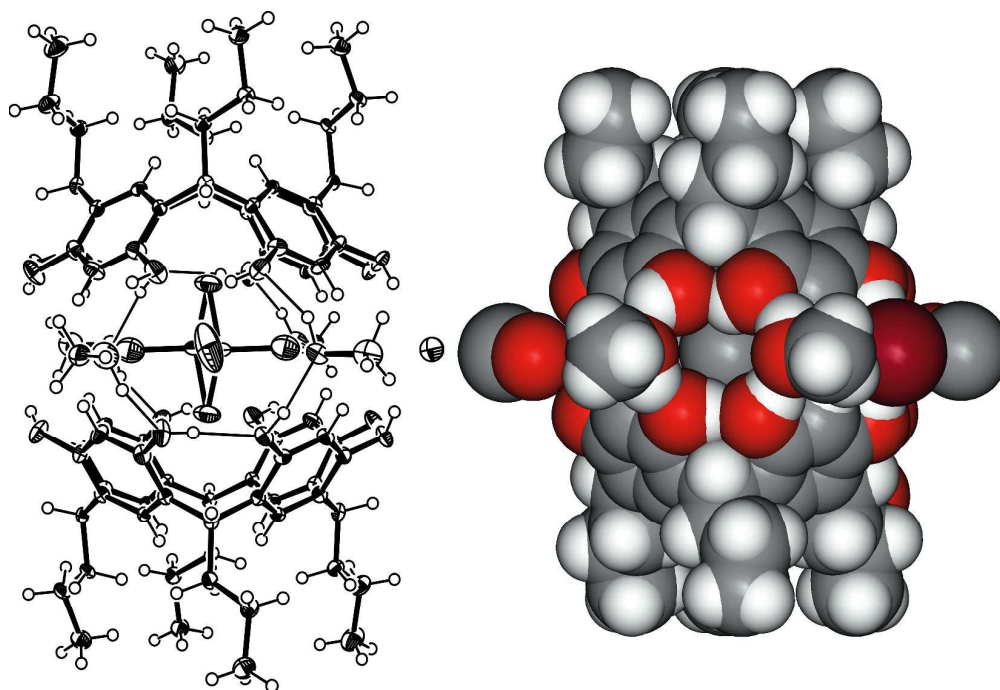


Figure 3
279x190mm (300 x 300 DPI)

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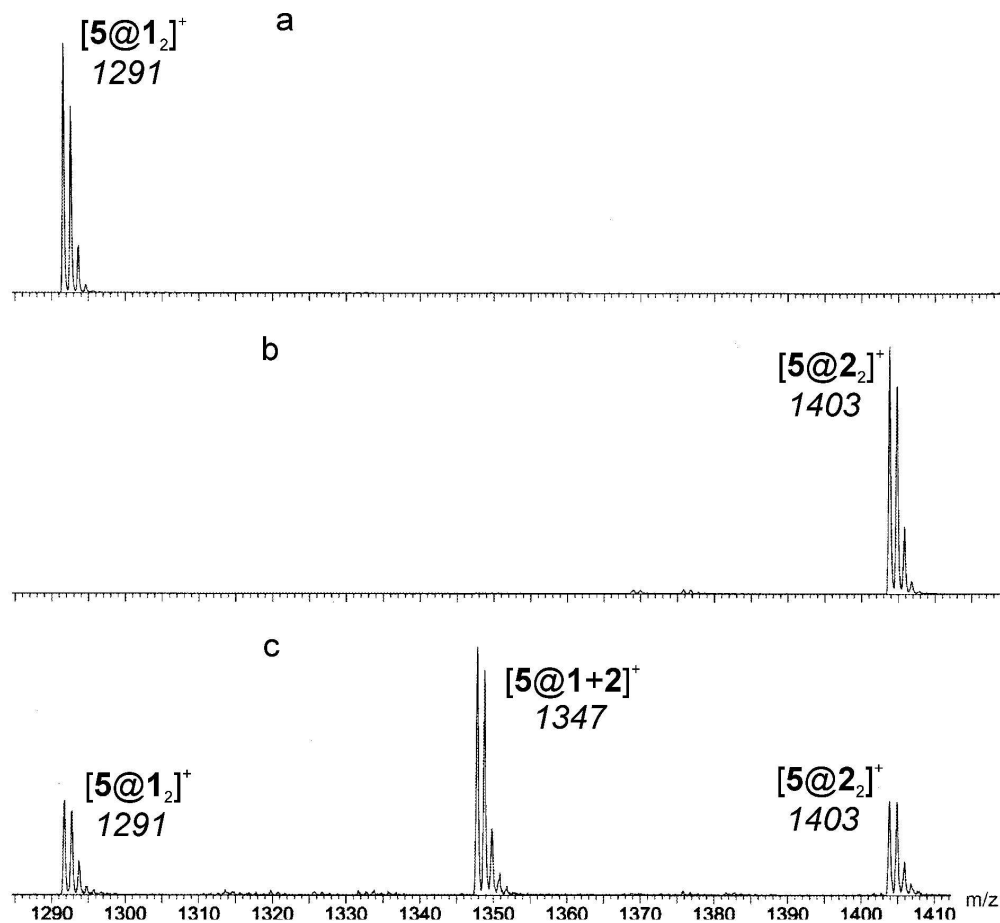


Figure 4
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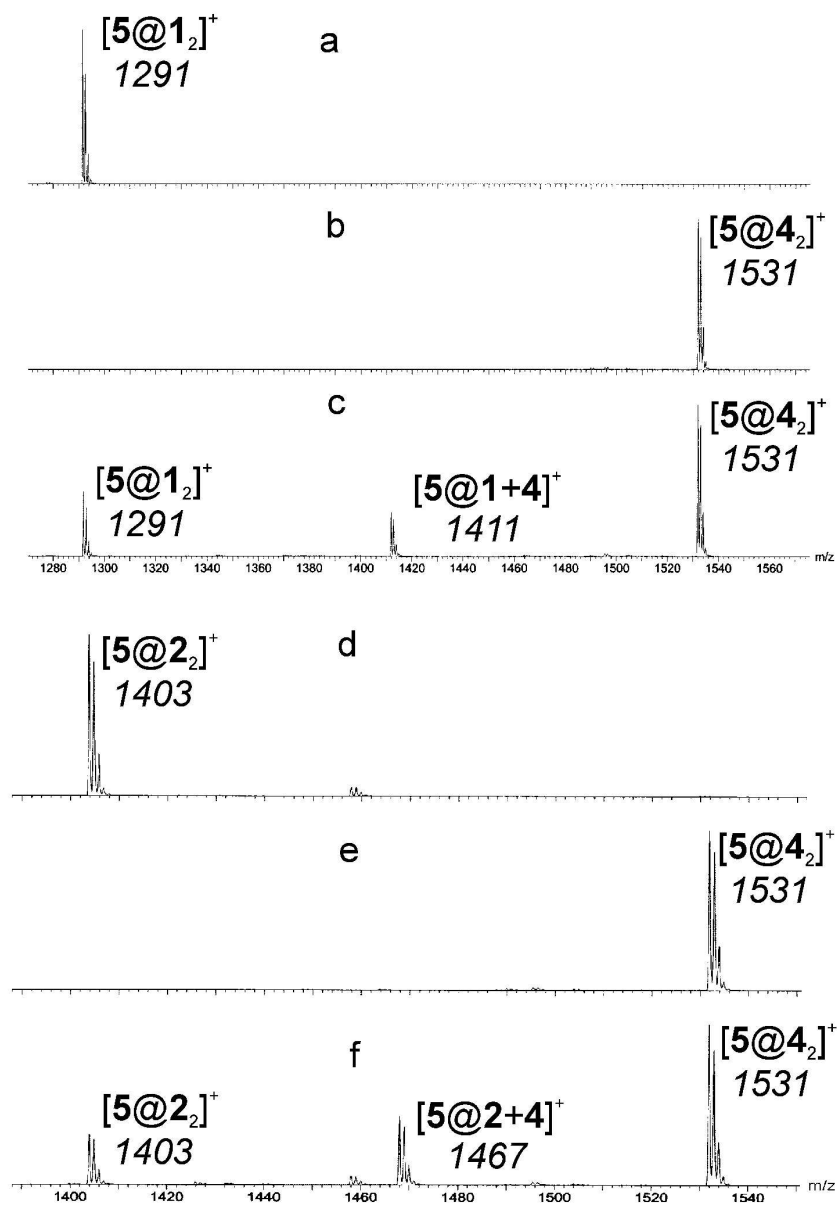


Figure 5
152x210mm (500 x 500 DPI)