

Water-Soluble Molecular Capsule for the Complexation of Cesium and Thallium Cations

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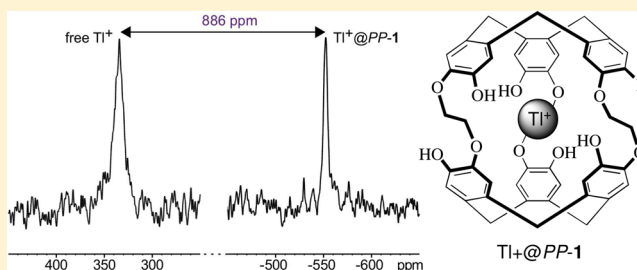
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S Supporting Information

ABSTRACT: Binding properties of cesium and thallium cations by an enantiopure cryptophane derivative PP-1 have been investigated in water under basic conditions. The binding process has been evidenced using electronic circular dichroism (ECD), and binding constants of the $\text{Cs}^+@PP-1$ and $\text{Tl}^+@PP-1$ complexes have been determined from isothermal titration calorimetry (ITC) experiments in $\text{LiOH}/\text{H}_2\text{O}$, $\text{NaOH}/\text{H}_2\text{O}$, and $\text{KOH}/\text{H}_2\text{O}$ solutions. In addition, $\text{Tl}^+@PP-1$ complex has been characterized for the first time by ^{205}Tl NMR spectroscopy. Cryptophane 1 exhibits an exceptionally high affinity for thallium and cesium cations in a large range of experimental conditions (nature, concentration of the counterion, and temperature). For example, binding constants as high as $2.9 \times 10^9 \text{ M}^{-1}$ and $5.3 \times 10^8 \text{ M}^{-1}$ have been measured by ITC at 298 K in $\text{NaOH}/\text{H}_2\text{O}$ (0.1 M) solution, for the $\text{Tl}^+@PP-1$ and $\text{Cs}^+@PP-1$ complexes, respectively. The high affinity of cryptophane 1 for Cs^+ and Tl^+ cations is preserved at higher LiOH , NaOH , and KOH concentrations and under extreme basic conditions, revealing the stability and the great selectivity of this supramolecular system toward Li^+ , Na^+ , and K^+ cations.



INTRODUCTION

The synthesis of molecular ligands showing good affinity for ionic species represents an important field of research in modern supramolecular chemistry. Indeed, the encapsulation of cations is of great interest because it finds applications in analytical chemistry, in biology, and in environmental chemistry.¹ For instance, supramolecular hosts able to detect highly toxic species in very low concentration, such as thallium(I), or to encapsulate radioactive elements (essentially $^{137}\text{Cs}^+$) are highly desirable. Thus, for several decades, chemists have synthesized and investigated numerous supramolecular systems, such as crown ethers and calixarenes, able to complex these cations.² These host molecules are generally soluble in organic solvents, and some of them exhibit large binding constant with the Cs^+ cation.^{2e,h,j,k,q} These compounds bear oxygen atoms within their structure, which can interact with the cation (crown-ether derivatives) or several aromatic rings aimed at stabilizing the complex via π -cation interactions (calixarene derivatives). Very recently, we have shown that the chiral cryptophane 1 (see Scheme 1) possessing either five hydroxyl

groups and six aromatic rings offers to chemists a new basic structure for the encapsulation of alkali cations.³

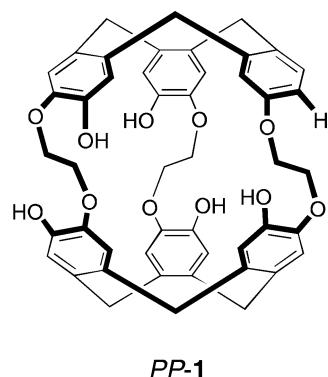
Since the first synthesis of the cryptophane derivatives, reported in the early 80s, these molecular capsules have demonstrated interesting binding properties toward small neutral molecules (methane and halomethanes), soft organic cations such as ammonium guest, organic anions, and even neutral atoms such as xenon or radon.⁴ This feature is the consequence of the spherical structure of cryptophanes that creates a lipophilic cavity suitable for accommodating guest molecules. The specific molecular recognition of these supramolecular hosts is mainly determined by the internal volume of the cavity that, in turn, is controlled by the length of the aliphatic linkers that connect the two cyclotribenzylene (CTB) caps (81, 95, and 121 \AA^3 for methylenedioxy, ethylenedioxy, and propylenedioxy linkers, respectively). Thus, cryptophane with ethylenedioxy linkers (i.e., crypto-

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Scheme 1. Structure of Water-Soluble Cryptophane 1; Only a Single Enantiomer (PP) Is Shown



phane-A derivatives) is appropriate to encapsulate a large range of small molecules or atoms whose maximum volume is about 70–75 Å³. Even though the guest–host molecular volume ratio is an important parameter in the binding process, Coulombic and electrostatic (π -cation) interactions can also contribute to the stabilization of the complexes with charged species. These kinds of interactions can explain the highly efficient and selective binding of rubidium (13.3 Å³) and cesium (19.5 Å³) cations by water-soluble cryptophane 1 in LiOH/H₂O solution.³ Another more specific interaction, due to the chiral nature of both the host and guest molecules, can occur since the inherently chiral cryptophane 1 is also able to discriminate between the two enantiomers of propylene oxide.⁵

The chiroptical properties of enantiopure cryptophanes and the molecular recognition of chiral or achiral guest molecules can be investigated by chiroptical techniques, such as polarimetry, electronic circular dichroism (ECD), and vibrational circular dichroism (VCD).⁶ The results obtained by these techniques have revealed that the chiroptical properties of cryptophane-A derivatives are strongly dependent on some external parameters such as the nature of the solvent (organic or aqueous) and the ability of a guest molecule to enter the cavity. Thus, significant and specific VCD and ECD responses upon complexation have been observed for water-soluble penta-hydroxyl and hexa-hydroxyl cryptophanes under basic conditions that depend on both the size of the guest and the nature of the counterion (Li⁺, Na⁺, K⁺, and Cs⁺) present in the solution.^{6d,e} Indeed, spectral modifications are clearly observed in the ¹L_b and the ¹B_b region of the ECD spectra, in LiOH/H₂O or NaOH/H₂O solutions, for guest molecules having different molecular volume ranging from $V_{\text{vdw}} = 42$ Å³ (chloromethane) to $V_{\text{vdw}} = 72$ Å³ (chloroform). Similarly, spectral modifications have been also observed in the VCD spectra, in particular the increase of the VCD intensity with the size of the guest molecules. These spectral modifications have been interpreted from molecular dynamics (MD) and ab initio calculations at the density functional theory (DFT) level by subtle conformational changes of the three linkers upon complexation. Thus, it has been shown that the guest-free cryptophane favors the *gauche* conformation of the linkers in order to reduce the size of the cavity (hydrophobic effect), whereas the filled cryptophane favors the *trans* conformation of the bridges when large guest molecules, such as chloroform enter its cavity. In contrast, no change of the VCD and ECD spectra is observed in CsOH/H₂O solution in the presence of a large excess of a guest molecule due to the high affinity of the

Cs⁺ cation for the cavity of penta-hydroxyl and hexa-hydroxyl cryptophanes.

In this article, we wish to investigate in detail the complexation of the monovalent cations Cs⁺ and Tl⁺ with the PP enantiomer of cryptophane 1. Several parameters, such as the nature of the solvent (LiOH/H₂O, NaOH/H₂O, and KOH/H₂O), the nature of the counterion of the monovalent cations, the concentration of the basic solution, and the effect of the temperature, have been investigated. The binding process between host 1 and these two cations has been evidenced by ECD spectroscopy. Additional experiments have been performed by VCD to confirm the conformational changes of the linkers. The high affinity of cryptophane 1 for Tl⁺ has been also revealed for the first time by ²⁰⁵Tl NMR spectroscopy. Finally, isothermal titration calorimetry (ITC) experiments have been performed to provide quantitative information about the encapsulation of Cs⁺ and Tl⁺ cations by cryptophane 1 under various conditions and to define the nature of the interactions between the cations and the host. The most probable structures of Cs⁺@PP-1 and Tl⁺@PP-1 complexes have been derived from DFT calculations.

■ EXPERIMENTAL SECTION

Synthesis of Enantiopure Penta-Hydroxyl Cryptophane 1. The synthetic route used to obtain enantiopure penta-hydroxyl cryptophane 1 has been previously reported.^{6c} This procedure has been followed to obtain the PP enantiomer in fair quantities with a very high enantiomeric excess (ee = 99–100%). A particular attention has been paid to the purification of PP-1 for ECD and ITC experiments.

UV–Vis and ECD Measurements. UV–vis and ECD spectra were recorded at 293 K, using a 0.2, 0.5, or 1 cm path length quartz cell. The concentration of PP-1 was in the range 10^{−5} M in basic H₂O solutions (0.1 M solutions of LiOH, NaOH, and KOH). Additional ECD spectra were recorded at different LiOH/H₂O concentrations (from 0.001 to 1 M) and in a solution containing a mixture of LiOH (1 M), NaOH (1 M), and KOH (1 M) solution. Spectra were recorded in the 220–400 nm wavelength range with a 0.5 nm increment and a 1 s integration time. Spectra were processed with standard spectrometer software and baseline corrected without smoothing. Spectral units were expressed in molar ellipticity.

IR and VCD Measurements. The infrared and VCD spectra were recorded with a FTIR spectrometer equipped with a VCD optical bench.⁷ IR absorption and VCD spectra were recorded at a resolution of 4 cm^{−1}, by coadding 50 scans and 24 000 scans (8 h acquisition time), respectively. Samples were held in a CaF₂ cell with a fixed path length of 45 μm. IR and VCD spectra of PP-1 were measured in basic NaOD/D₂O (0.21 M) solutions at a concentration of 0.030 M in the presence of a very small amount of CDCl₃ and Cs⁺ cation (~1 equiv [host]). Baseline corrections of the VCD spectra were performed by subtracting the two opposite-enantiomer VCD spectra of 1 (recorded under the same experimental conditions) with division by two. In all experiments, the photoelastic modulator was adjusted for a maximum efficiency at 1400 cm^{−1}. Calculations were done with the standard spectrometer software, using Happ and Genzel apodization, de-Haseth phase-correction, and a zero-filling factor of 1. Calibration spectra were recorded using a birefringent plate (CdSe) and a second BaF₂ wire grid polarizer, following the experimental procedure previously published.⁸ Finally, in the presented IR spectra, the solvent absorption was subtracted out.

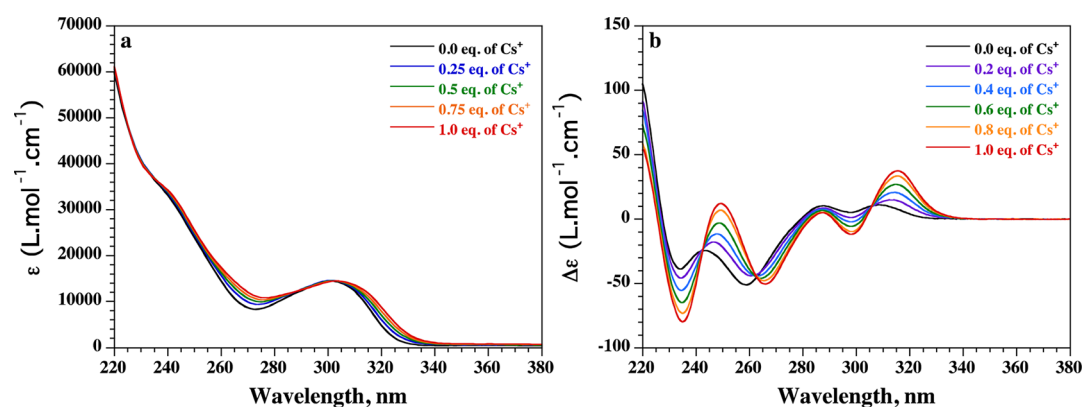


Figure 1. (a) UV-vis spectra recorded at 293 K of empty *PP-1* ([host] 1.46×10^{-5} M, path length of 0.5 cm) and $\text{Cs}^+@PP-1$ complex in LiOH/H₂O solution (0.1 M). (b) ECD spectra recorded at 293 K of *PP-1* ([host] from 7.53 to 8.31×10^{-5} M, path length of 0.2 cm) in LiOH/H₂O solution (0.1 M) in the presence of different amounts of cesium hydroxide solution. ECD spectra for higher $[\text{Cs}^+]$ are identical to that recorded for 1 equiv of Cs^+ .

ITC Experiments. Isothermal Titration Calorimetry (ITC) experiments were performed at 298 K. In a standard experiment, the host solution (~ 0.1 mM) in LiOH (0.1 M), NaOH (0.1 M), or KOH (0.1 M) was placed into the calorimeter cell (1.4 mL), and 28 successive aliquots (10 μL) of guest solution (10 times more concentrated) were added via a computer-automated injector at 3 min intervals. Heat changes were recorded after each addition. Heats of dilution were measured by a blank experiment (in absence of host) under the same conditions, and they were subtracted from the titration data prior to curve fitting. The first injection was discarded from each data set to remove the effect of guest diffusion across the syringe tip during the equilibration process. Titrations curves were fitted with the one binding site model. Additional ITC experiments have been performed at lower (0.0025 and 0.02 M) or higher (0.5 and 1 M) LiOH concentrations under the same conditions.

^{205}Tl RMN Experiments. The ^{205}Tl NMR experiments were performed on a Bruker DMX300 spectrometer (7 T) equipped with a 5 mm BB Nalorac probehead recovered from an 11.7 T spectrometer. First, a solution of thallium nitrate was used as a chemical shift reference (0 ppm). Then, the other spectra were recorded by part. At 308 K, thallium (TlOAc in water) resonated at 173.183957 MHz, while thallium encapsulated in cryptophane *PP-1* resonated at 173.030506 MHz, giving a chemical shift difference of 886 ppm. The spectral selectivity (linked to the transmitter power) enabled us to decrease the interscan delay for the acquisition of the bound thallium signal, playing with the fast exchange in and out of the cryptophane cavity. A frequency-selective inversion-recovery experiment was employed to estimate the exchange rate. The extracted value was on the order of 1200 s^{-1} at 308 K.

DFT Calculations. The geometry optimizations, vibrational frequencies, and absorption intensities were calculated by the Gaussian09 program⁹ on the DELL cluster of the MCIA computing center of the University Bordeaux I. Calculations of the optimized geometry of $\text{Cs}^+@PP-1$ and $\text{Ti}^+@PP-1$ complexes were performed at the density functional theory level using CAM-B3LYP functional and 6-31+G* basis set, except for the Cs^+ and Ti^+ cations for which LAND2Z basis set was used. DFT calculations were performed considering the phenolate (O^-Li^+ peripheral substituents) form of the molecule with the *GTT* conformation of the three $-\text{OCH}_2\text{CH}_2\text{O}-$ bridges. Additional calculations of the optimized geometry of

empty *PP-1*, $\text{Cs}^+@PP-1$, and $\text{CDCl}_3@PP-1$ complexes were performed at the B3PW91/6-31G* level, considering the phenol (OD peripheral substituents) form of the molecule for the *GGG*, *GTT*, and *TTT* conformations of the three linkers. Vibrational frequencies and IR intensities were calculated at the same level of theory.

RESULTS

Complexation of Cesium Cations. The complexation of the cesium cation by enantiopure cryptophane *PP-1* has been first investigated in LiOH/H₂O solution at 293 K using an arbitrary concentration of 0.1 M. Different salts such as cesium acetate (CsOAc), cesium hydroxide (CsOH), and cesium carbonate (Cs_2CO_3) have been used in this study. The UV-vis and ECD spectra of empty *PP-1* and *PP-1* in the presence of cesium hydroxide are reported in Figure 1 in the 220–380 nm spectral range. The UV-vis spectra (Figure 1a) exhibit a strong absorption band below 220 nm corresponding to the allowed $^1\text{B}_u$ transition (Platt's notation) of the benzene rings and two absorption bands of medium intensity around 240 and 300 nm corresponding to the two forbidden $^1\text{L}_a$ and $^1\text{L}_b$ transitions of the benzene rings, respectively. The UV-vis spectrum of empty *PP-1* is slightly modified by the addition of cesium hydroxide, involving a bathochromic shift of the $^1\text{L}_a$ and $^1\text{L}_b$ transitions. However, Figure 1b shows that the addition of various quantities of a cesium hydroxide solution to the LiOH/H₂O solution of guest free host **1** gives rise to a significant change of the overall ECD spectrum in the 220–380 nm region. Spectral modifications are detected in the 290–330 nm region of the ECD spectrum corresponding to the $^1\text{L}_b$ transition of the benzene rings. It is observed that increasing the amount of cesium cations from 0 to 1 equivalent [host **1**] induces an increase of the ECD component located at 315 nm and a decrease of the component located at 300 nm. In addition, large spectral changes are also observed at 220 nm corresponding to the $^1\text{B}_u$ transition of the benzene rings. Indeed, increasing the amount of cesium into the solution gives rise to a strong decrease of the rotational strength of this band going from $\Delta\epsilon = 100\text{ L mol}^{-1}\text{ cm}^{-1}$ for the guest free host to $\Delta\epsilon = 50\text{ L mol}^{-1}\text{ cm}^{-1}$ when 1 equiv of cesium has been added to the solution. Addition of more than 1 equiv of Cs^+ does not modify the overall ECD spectrum of host **1**. It is noteworthy that the presence of the three isosbestic points in Figure 1b is due to the apparition of a new species, which can be attributed to the

Cs⁺@PP-1 complex. Finally, the replacement of CsOH solution, by CsOAc or Cs₂CO₃ solutions, leads to similar ECD spectra in the same experimental conditions (Supporting Information, Figure 1).

The effect of the LiOH concentration on the ECD spectrum of PP-1 in the absence or in the presence of cesium hydroxide has been examined (Supporting Information, Figure 2). At a concentration of 0.001 M, which is the minimal concentration to solubilize host **1**, the evolution of the ECD spectra in the presence of various amounts of Cs⁺ cations is very similar to that observed at 0.0025 M. It is noteworthy that the intensity of the ECD band associated with the ¹B_b transition, located at 220 nm, is lower than $\Delta\epsilon = 38 \text{ L mol}^{-1} \text{ cm}^{-1}$. At higher LiOH concentrations, we observe an enhancement of the intensity of this band in the absence of cesium hydroxide (empty PP-1), which reaches a value of $\Delta\epsilon = 100, 200$, and $230 \text{ L mol}^{-1} \text{ cm}^{-1}$ for 0.1, 0.5, and 1 M LiOH concentrations, respectively. It can be noticed that, when 1 equivalent of Cs⁺ is added to host PP-1, the ECD spectra recorded at 0.5 and 1 M [LiOH] are identical to that measured at 0.1 M. In this case, the ECD band associated with the ¹B_b transition is approximately $\Delta\epsilon = 60 \text{ L mol}^{-1} \text{ cm}^{-1}$. Thus, the addition of a cesium hydroxide in LiOH/H₂O solutions (>0.1 M) containing host **1** results in a significant decrease in intensity of the ECD band located at 220 nm.

The nature of the basic solution used to dissolve the water-soluble cryptophane **1** was also studied in this article. For instance, when host **1** is dissolved in a NaOH/H₂O (0.1 M) solution, the ECD spectrum of empty PP-1 is very similar to that obtained in LiOH/H₂O (0.1 M) and the addition of cesium cations results in similar effects (Supporting Information, Figure 3). In contrast, when NaOH/H₂O (0.1 M) is replaced by a KOH/H₂O (0.1 M) solution, the ECD spectrum of empty PP-1 is slightly modified by the addition of small quantities of cesium hydroxide solution, and only a very small bathochromic shift is observed in Figure 2.

Finally, ECD spectra of PP-1 in LiOH/H₂O (1 M) solution were recorded at 278, 293, and 343 K to investigate the effect of the temperature. The spectral modifications observed on the ECD spectra upon the addition of Cs⁺ cations are similar for the three temperatures (Supporting Information, Figure 4).

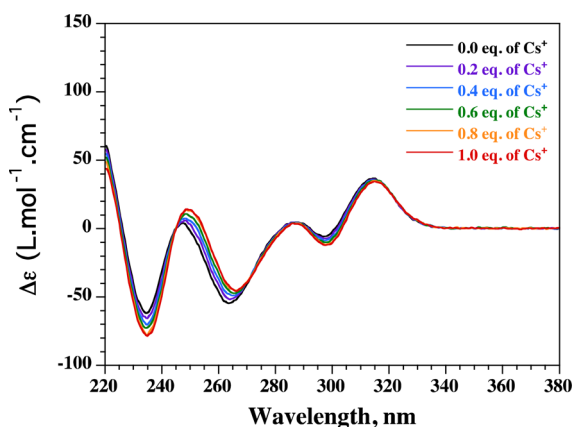


Figure 2. ECD spectra recorded at 293 K of PP-1 ($[\text{host}] = 1.12 \times 10^{-5} \text{ M}$, path length of 1.0 cm) in KOH/H₂O solution (0.1 M) in the presence of different amounts of cesium hydroxide solution. ECD spectra for higher [Cs⁺] are identical to that recorded for 1 equiv of Cs⁺.

However, at 343 K, the addition of more than 1 equiv of Cs⁺ still produces a modification of the ECD spectrum of PP-1, in contrast to what is observed at lower temperatures or at lower LiOH concentration (0.1 M).

Isothermal titration calorimetry (ITC) has been used in this study to provide quantitative information about the encapsulation of cesium cations by PP-1. ITC experiments have been performed at 298 K by varying the nature and the concentration of the basic solution (LiOH/H₂O, NaOH/H₂O, and KOH/H₂O). Experiments have been performed twice to estimate the experimental error on the binding constant K . As mentioned previously,³ the accurate measurement of the binding constant for the Cs⁺@PP-1 complex in LiOH/H₂O and NaOH/H₂O solutions cannot be achieved from the direct ITC measurement between cesium hydroxide solution and guest free host **1**. Indeed, the high affinity of Cs⁺ cation for host **1** (i.e., K values higher than 10^8 M^{-1}) requires the determination of K from competition experiments, using another cation having a lower affinity (K values around 10^5 M^{-1}) for host **1**. Hopefully, the Rb⁺ cation satisfies this condition, and its binding constants have been determined by ITC experiments at 298 K in LiOH/H₂O ($K = 1.29 \times 10^5 \text{ M}^{-1}$), NaOH/H₂O ($K = 1.71 \times 10^5 \text{ M}^{-1}$), and KOH/H₂O ($K = 7200 \text{ M}^{-1}$) solutions at an arbitrary concentration of 0.1 M (Supporting Information, Figure 5). ITC experiments for Cs⁺@PP-1 complex in LiOH/H₂O (0.1 M), NaOH/H₂O (0.1 M), and KOH/H₂O (0.1 M) solutions are reported in the Supporting Information (Figures 6–8), and the thermodynamic parameters of complexation are summarized in Table 1.

Table 1. Thermodynamic Parameters of Complexation for Cs⁺@PP-1 and Tl⁺@PP-1 Complexes in LiOH/H₂O (0.1 M), NaOH/H₂O (0.1 M), and KOH/H₂O (0.1 M) Solutions at 298 K: Binding Constant K (M^{-1}), Enthalpy ΔH (kcal mol^{-1}), Entropy ΔS (cal $\text{mol}^{-1} \text{ deg}^{-1}$), and ΔG (kcal mol^{-1}) of Complexation

solution	cation	K	ΔH	ΔS	ΔG
LiOH/H ₂ O ^a	Cs ⁺	$3.80 \times 10^8 \pm 0.04 \times 10^8$	−12.9	−4.1	−11.7
NaOH/H ₂ O ^a	Cs ⁺	$5.30 \times 10^8 \pm 0.04 \times 10^8$	−12.9	−3.3	−11.9
KOH/H ₂ O ^a	Cs ⁺	$2.20 \times 10^7 \pm 0.22 \times 10^7$	−8.5	+5.0	−10.0
LiOH/H ₂ O ^a	Tl ⁺	$2.39 \times 10^9 \pm 0.05 \times 10^9$	−12.7	+0.4	−12.8
NaOH/H ₂ O ^a	Tl ⁺	$2.86 \times 10^9 \pm 0.11 \times 10^9$	−12.7	+0.7	−12.9
KOH/H ₂ O ^a	Tl ⁺	$1.33 \times 10^8 \pm 0.30 \times 10^8$	−8.0	+10.4	−11.1

^aFrom competition experiments.

Binding constant values around $5 \cdot 10^8 \text{ M}^{-1}$ have been obtained for the Cs⁺@PP-1 complex in LiOH/H₂O and NaOH/H₂O solutions, whereas the K value is one order lower in KOH/H₂O solution.

The effect of the LiOH concentration on the complexation has also been investigated. Unfortunately, the host concentration used for ITC experiments does not allow us to work below a concentration of 0.0025 M in LiOH/H₂O solution, which is the minimal concentration to dissolve host **1**. The ITC experiments performed at different LiOH concentration are reported in Supporting Information (Figures 9–12) and the thermodynamic parameters of complexation are summarized in Table 2. Globally, the value of the binding constant decreases for Cs⁺@PP-1 complex when the LiOH concentration increases.

Table 2. Thermodynamic Parameters of Complexation for Cs⁺@PP-1 and Tl⁺@PP-1 Complexes Measured at 298 K in LiOH/H₂O Solution with Various Concentration of LiOH

[LiOH]	cation	<i>K</i>	ΔH	ΔS	ΔG
0.0025 M ^a	Cs ⁺	$6.24 \times 10^8 \pm 0.03 \times 10^8$	−17.2	−17.6	−12.0
0.02 M ^a	Cs ⁺	$9.21 \times 10^8 \pm 0.39 \times 10^8$	−14.3	−7.0	−12.2
0.1 M ^a	Cs ⁺	$3.80 \times 10^8 \pm 0.04 \times 10^8$	−12.9	−4.1	−11.7
0.5 M ^a	Cs ⁺	$3.02 \times 10^7 \pm 0.09 \times 10^7$	−12.8	−8.6	−10.2
1 M ^b	Cs ⁺	$9.28 \times 10^6 \pm 0.15 \times 10^6$	−12.4	−9.6	−9.5
0.0025 M ^a	Tl ⁺	$2.73 \times 10^9 \pm 0.18 \times 10^9$	−17.3	−15.0	−12.8
0.02 M ^a	Tl ⁺	$6.03 \times 10^9 \pm 0.21 \times 10^9$	−13.9	−1.8	−13.4
0.1 M ^a	Tl ⁺	$2.39 \times 10^9 \pm 0.05 \times 10^9$	−12.7	+0.4	−12.8
0.5 M ^a	Tl ⁺	$2.10 \times 10^8 \pm 0.05 \times 10^8$	−11.3	+0.2	−11.4
1 M ^b	Tl ⁺	$7.00 \times 10^7 \pm 0.66 \times 10^7$	−11.0	−0.8	−10.8

^aFrom competition experiments. ^bFrom direct measurements.

Complexation of Thallium Cations. Our recent study showing the complexation of alkali cations such as K⁺, Rb⁺, and Cs⁺ by water-soluble cryptophane **1** prompted us to investigate the possible encapsulation of other monovalent or divalent cations.³ Unfortunately, the basic conditions used to dissolve **1** are not suitable for the dissolution of salts of divalent cations. Indeed, most of them give rise to insoluble hydroxide derivatives. Nevertheless, we found that thallium salts were able to dissolve easily under these basic conditions. Thus, thallium nitrate and thallium acetate have been used for the ECD and ITC experiments.

The UV–vis and ECD spectra of PP-1 in LiOH/H₂O (0.1 M) in the presence of various quantities of TlOAc solution are reported in Figure 3. As previously observed for cesium salts, the addition of small amounts of thallium solution to the LiOH/H₂O solution of guest free host **1** gives rise to a significant change of the UV–vis and ECD spectra in the 220–380 nm region. As shown in Figure 3a, these spectral changes are more marked for the complexation of thallium cations. The presence of isosbestic points in Figure 3b clearly indicates the apparition of a new species, which can be attributed to the Tl⁺@PP-1 complex. The intensity of the ¹B_u band decreases upon the addition of a TlOAc solution, as previously observed for cesium salts. The ¹L_b band above 280 nm seems more strongly affected by the presence of Tl⁺@PP-1 complex than by the presence of Cs⁺@PP-1 complex. In addition, a significant bathochromic shift is observed upon increasing to 1 equiv of

the amount of thallium salt into the solution, but no additional spectroscopic changes are observed for higher concentration of Tl⁺ cations. Finally, the replacement of a TlOAc solution, by a TlNO₃ solution, leads to similar ECD spectra in the same experimental conditions (Supporting Information, Figure 13).

The ECD spectra recorded at different LiOH concentrations (between 0.001 to 1 M) show important modifications of the spectra upon the addition of Tl⁺ cations. As observed for the Cs⁺@PP-1 complex, these spectral modifications are more marked for higher LiOH concentrations, in particular in the 220–245 nm region. Indeed, for the LiOH/H₂O (1 M) solution, the ECD band located at 220 nm decreases strongly with the addition of Tl⁺ cations (Supporting Information, Figure 14). In contrast, the change of the nature of the solvent produces only small spectral modifications. For instance, LiOH/H₂O (1 M), NaOH/H₂O (1 M), and KOH/H₂O (1 M) solutions give similar ECD spectra for the guest free host **1** or upon the addition of thallium nitrate (Supporting Information, Figure 15). Finally, it is noteworthy that, under more drastic conditions (solution containing a mixture of LiOH (1 M), NaOH (1 M) and KOH (1 M)), the addition of thallium salt still produces a modification of the ECD spectrum of guest free PP-1 in the 260–400 nm region (Supporting Information, Figure 16). However, in contrast to what is observed at lower ionic strength, the addition of 2 or 4 equiv of Tl⁺ cation induces spectral modifications and, in particular, leads to an increase of the two ECD bands located at 295 and 320 nm.

As previously reported for the cesium cations, ITC experiments have been performed under various experimental conditions to quantify the interaction between the thallium cation and the cavity of host **1**. Since direct measurements achieved with thallium salt and host PP-1 were found too inaccurate in LiOH/H₂O, NaOH/H₂O, and even KOH/H₂O solutions, competition experiments between thallium and rubidium have been performed at 298 K. The effect of the nature of the basic solution has been first investigated. ITC experiments for Tl⁺@PP-1 complex in LiOH/H₂O (0.1 M), NaOH/H₂O (0.1 M), and KOH/H₂O (0.1 M) solutions are reported in the Supporting Information (Figures 17–19), and the thermodynamic parameters of complexation are summarized in Table 1. Binding constant values in the range 2–3 × 10⁹ M^{−1} have been obtained for Tl⁺@PP-1 complex in LiOH/H₂O and NaOH/H₂O solutions, whereas the *K* value decreases by 1

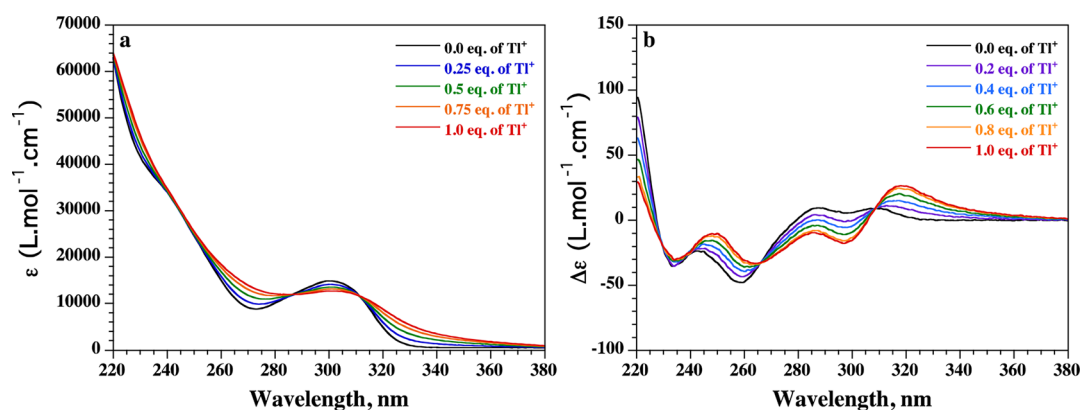


Figure 3. (a) UV–vis spectra recorded at 293 K of empty PP-1 ([host] 1.43×10^{-5} M, path length of 1 cm) and Tl⁺@PP-1 complex in LiOH/H₂O solution (0.1 M). (b) ECD spectra recorded at 293 K of PP-1 ([host] = 1.34×10^{-5} M) in LiOH/H₂O solution (0.1 M) in the presence of different amounts of thallium acetate solution. ECD spectra for higher [Tl⁺] are identical to that recorded for 1 equiv of Tl⁺.

order of magnitude ($K = 1 \cdot 10^8 \text{ M}^{-1}$) in KOH/H₂O solution. Then, ITC experiments have been performed at different LiOH concentrations (Supporting Information, Figures 20–23), and the thermodynamic parameters of complexation are summarized in Table 2. As observed for the Cs⁺@PP-1 complex, the value of the binding constant decreases when the LiOH concentration increases.

Finally, ²⁰⁵Tl NMR spectroscopy has been used to characterize the Tl⁺@PP-1 complex. Thallium NMR was developed as a method for determining the relative stability of thallium complexes with a range of crown ethers and to probe the solvent dependence of complexation in thallium cryptates.¹⁰ More recently, thallium NMR has been applied to show the presence of π -cation interactions between thallium and calix[4]arene derivatives^{20,t} and to investigate the solvent effects on thermodynamic and kinetic properties of the complexation of a macrocyclic ligand (18-crown-6).^{2u} ²⁰⁵Tl NMR spectroscopy has demonstrated its high sensitivity since small changes in environment greatly affect the thallium resonance signal, enabling clear and direct observation of the complexation process. Here, because of the ring current effect of the cryptophane, a strong high-field shift is expected for the Tl⁺@PP-1 complex with respect to the Tl⁺ cation present in solution.

NMR experiments have been performed on the most abundant isotope ²⁰⁵Tl, which is the easiest to detect by NMR spectroscopy. The NMR spectrum of a solution containing a millimolar concentration of PP-1 in NaOD/D₂O (0.1 M) solution in the presence of a trace of thallium acetate is reported in Figure 4. This ²⁰⁵Tl NMR spectrum reveals a large

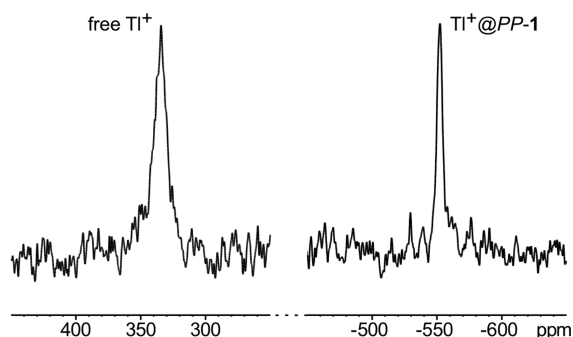


Figure 4. ²⁰⁵Tl NMR spectrum recorded at 298 K of PP-1 (1.23 mg) in NaOD/D₂O (0.5 mL; 0.1 M) solution in the presence of a small amount (1 mg) of thallium acetate.

signal located at +330 ppm (reference TlNO₃ in D₂O), which is assigned to the free ²⁰⁵Tl⁺ cation dissolved in solution. Shifting the transmitter frequency reveals a second sharp ²⁰⁵Tl⁺ NMR signal, located at lower frequency ($\delta = -556 \text{ ppm}$), which is assigned to the ²⁰⁵Tl⁺@PP-1 complex. Remarkably, this signal is still easily detectable at 353 K and the half-width does not change significantly from 353 to 278 K (Supporting Information, Figure 24).

DISCUSSION

Conformational Changes of PP-1 upon Encapsulation of Cesium and Thallium Cations. In previous articles, we have shown that ECD spectroscopy is a very valuable technique to investigate the complex formation between guest molecules and some water-soluble cryptophanes.^{6d,e} In particular, we have shown that the ECD band located at 220 nm, assigned to the

¹B_b transition of the benzene rings, has its intensity significantly modified depending on the size of the neutral guest molecule trapped inside the cavity of the cryptophane. Thus, large neutral molecules such as chloroform ($V_{\text{vdw}} = 72 \text{ \AA}^3$) encapsulated inside the cavity of PP-1 lead to a significant increase of this band ($\Delta\epsilon = 190 \text{ L mol}^{-1} \text{ cm}^{-1}$). In turn, small neutral molecules such as chloromethane ($V_{\text{vdw}} = 42 \text{ \AA}^3$) exhibit ECD signal with a lower intensity ($\Delta\epsilon = 110 \text{ L mol}^{-1} \text{ cm}^{-1}$), which is very close to that observed for the empty PP-1 ($\Delta\epsilon = 100 \text{ L mol}^{-1} \text{ cm}^{-1}$). These spectral modifications and those observed in the VCD spectra (in particular, the enhancement of the band located at 1490 cm^{-1} upon encapsulation of neutral molecules) have been directly correlated to the conformational changes of the three ethylenedioxy linkers.^{6c} Indeed, molecular dynamics (MD) and DFT calculations concluded that the *gauche*–*trans*–*trans* (GTT) conformation of the linkers is the most favorable one for the empty PP-1, whereas the presence of chloroform in the cavity of PP-1 favors the TTT conformation of the linkers. Moreover, the spectral modifications of the VCD spectra predicted by this conformational change are in perfect agreement with those observed experimentally, supporting our interpretation of the results. In this study, we show that ECD spectroscopy is also very useful to investigate the complex formation between cesium (or thallium) cation and host 1. Indeed, this technique reveals strong modifications on the ECD spectrum of Cs⁺@PP-1 and Tl⁺@PP-1 complexes, for which the intensity of the band located at 220 nm decreases significantly upon encapsulation of cesium ($\Delta\epsilon = 50 \text{ L mol}^{-1} \text{ cm}^{-1}$) and thallium ($\Delta\epsilon = 30 \text{ L mol}^{-1} \text{ cm}^{-1}$) cations. The spectral modifications observed on the ECD spectra of PP-1 upon the addition of cesium (or thallium) salt is also a consequence of the conformational changes of the three linkers that modifies the volume of the cavity of the host. A reduction of this volume is required to maximize the interaction between the cesium ($V = 19.5 \text{ \AA}^3$) or the thallium ($V = 14.1 \text{ \AA}^3$) cations and the cavity of the cryptophane. This reduction is only possible by the presence of *gauche* conformations of the linkers.¹¹ Thus, we believe that the complexation of cesium and thallium cations by PP-1 favors the *gauche* conformation of the linkers in order to reduce the size of the cavity. To confirm this assumption, we have recorded the VCD spectrum of Cs⁺@PP-1 complex in NaOD/D₂O (0.21 M) solution, for which a decrease of the VCD bands located at 1490 cm^{-1} is expected.^{6a,c} As shown in Figure 5, the intensity of this band decreases for Cs⁺@PP-1 complex. In addition, we observe strong spectral modifications in the 1400 – 1250 cm^{-1} region, which correspond to coupled modes involving wagging and twisting vibrations of the CH₂ groups (chains and caps). Since these modes are very sensitive to the conformation of the linkers, spectral changes in this region are also an evidence of the modification of the conformation of host 1.

Moreover, a closer examination of the IR spectra (Supporting Information, Figure 25a) reveals the presence of a band at 1368 cm^{-1} for the Cs⁺@PP-1 complex. This band is also observed in the IR spectrum of empty PP-1, with a lower intensity, whereas it is not present in the IR spectrum of the CDCl₃@PP-1 complex. In previous studies reported by Snyder^{12a} and Zerbi et al.,^{12b} an IR band around 1368 cm^{-1} has already been observed in molten polyethylene and had been attributed to methylene wagging vibration of polyethylene chains, which present *gauche* defects. Calculated IR spectra at the B3PW91/6-31G* level of empty PP-1 achieved for various conformers of the cryptophane confirm the presence of this band for the GGG

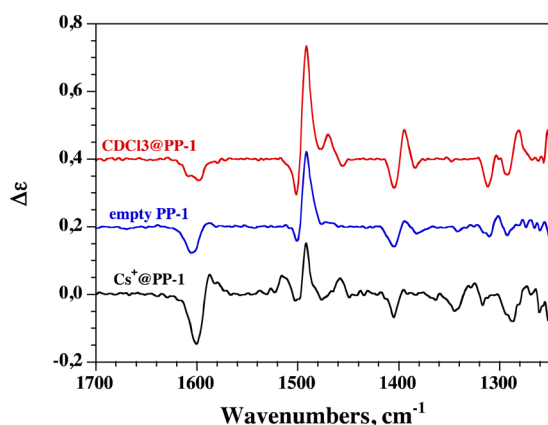


Figure 5. VCD spectra recorded at 293 K of empty *PP-1* as well as CDCl_3 @*PP-1* and Cs^+ @*PP-1* complexes in $\text{NaOD}/\text{D}_2\text{O}$ solution (0.21 M). The concentration of host **1** was 0.030 M.

conformation of the linkers, whereas this band is not calculated for the *TTT* conformation (Supporting Information, Figure 25c). This band is also calculated for the *GTT* conformation, but with a lower intensity. Similarly, we have observed that the IR band located at 1000 cm^{-1} , assigned to the symmetrical stretching vibration, $\nu_s(\text{C}-\text{O})$, of the $=\text{C}-\text{O}-\text{C}$ groups, is very sensitive to the conformation of the linkers (Supporting Information, Figure 25b). Indeed, this band is observed in the IR spectrum of the CDCl_3 @*PP-1* complex, whereas it vanishes in the IR spectrum of the Cs^+ @*PP-1* complex. DFT calculations confirm that the presence of this band is associated with the *trans* conformation of the linkers (Supporting Information, Figure 25d). Therefore, the 1368 and 1000 cm^{-1} bands could be used in the future to follow the conformational changes occurring on the cryptophane skeleton upon encapsulation of cations or neutral molecules.

The ECD results reveal also an interesting feature depending on the ionic strength of the solution. As observed in Supporting Information (Figure 2) in $\text{LiOH}/\text{H}_2\text{O}$ solution, the ECD spectra of the guest free *PP-1* are strongly modified when the concentration of LiOH increases. Thus, at low concentration, the ECD band located at 220 nm exhibits a very moderate intensity ($\Delta\epsilon = 15\text{ L mol}^{-1}\text{ cm}^{-1}$), whereas its intensity is strongly enhanced ($\Delta\epsilon > 200\text{ L mol}^{-1}\text{ cm}^{-1}$) for LiOH concentration higher than 0.5 M . Since the high intensity of this band has been previously associated with the presence of all-*trans* conformation of the linkers, we conclude that the presence of a large amount of Li^+ counterions in the solution favors the *trans* conformation of the linkers. To explain this surprising effect, we assume that the lithium counterions, which have a very limited affinity for the cavity of the host, interact more strongly with the oxygen atoms of the cryptophane (inducing a constraint on the cavity), favoring the *trans* conformation of the linkers. On the contrary, at low concentration of LiOH , the *gauche* conformation of the linkers is favored and the cryptophane tends to reduce the size of its cavity due to hydrophobic effects. This effect of the counterion concentration has an interesting consequence on the binding of cesium and thallium cations. Indeed, ECD experiments performed at various concentration of LiOH show very different behavior upon the addition of cesium or thallium cations. As expected at high LiOH concentration, the spectral modifications observed on the ECD spectra of **1** are large since the accommodation of the Cs^+ and TI^+ cations involves an

important conformational change of the host in order to maximize host–guest interactions. In contrast, at lower LiOH concentration, the preferential *gauche* conformation of the linkers creates a cavity, which is already well adapted (in size) for the complexation of cesium and thallium cations. Thus, this study shows that the binding of Cs^+ and TI^+ is less efficient at high LiOH concentration, not only because the lithium cations can compete with the Cs^+ (or TI^+) cations but also because the host **1** adopts a conformation of the linkers, which is less favorable for the complexation of cationic species. However, at very low LiOH concentration, the presence of residual hydroxyl function can also have a detrimental effect since we assume that Coulombic interactions contribute significantly to the stabilization of the Cs^+ @*PP-1* and the TI^+ @*PP-1* complexes. However, this assumption cannot be easily evidenced since host **1** is not soluble at neutral pH. Therefore, we believe that there is an optimal counterion concentration that favors host–guest interactions with these two cations.

Finally, the nature of the counterion of the cesium (or thallium) salt does not produce any change of the ECD spectrum of *PP-1*, suggesting that the counterion is located outside the cavity of the cryptophane and that ECD spectroscopy is only a characteristic of the interaction between the cation and the cavity of host **1**. This result differs from the ditopic molecular systems complexing Cs^+ reported previously in the literature.¹³

Host–Guest Interactions. The different behavior observed in the $^1\text{L}_b$ region of the UV–vis and ECD spectra for the Cs^+ @*PP-1* and TI^+ @*PP-1* complexes suggests that these two cations interact differently with the cavity of host **1**. Indeed, the spectral changes of the UV–vis and ECD spectra are more pronounced for the TI^+ @*PP-1* complex and are observed over a larger spectral range (up to 380 nm). This effect could be interpreted as the result of a stronger interaction between the TI^+ and the host molecule, as previously reported by Canet and co-workers.^{2r} These authors have clearly established, from NMR experiments, that the thallium cation has a higher interaction than the cesium cation with the cavity of a calixarene. They have explained this result considering the larger polarizability of the thallium cation, which is twice that of the cesium cation.¹⁴

The ITC experiments performed in this study confirm this assumption since the binding constant determined at 298 K for the TI^+ @*PP-1* complex ($K = 2.4 \times 10^9\text{ M}^{-1}$) is one order higher than that obtained for the Cs^+ @*PP-1* complex ($K = 3.8 \times 10^8\text{ M}^{-1}$). This last value is consistent with the previous binding constant reported at 278 K in the same condition.³ These two values of K are remarkable if we keep in mind that the binding process occurs in water and in the presence of a large excess of Li^+ cations. In addition, the ITC experiments show that the binding process is enthalpy controlled for the Cs^+ and the TI^+ cations. Indeed, the term $T\Delta S$ is very low, in particular, for the TI^+ @*PP-1* complex ($<0.2\text{ kcal mol}^{-1}$), and is certainly associated with the preorganized structure of the cryptophane backbone. The high value of the enthalpy of complexation ($\Delta H \approx -13\text{ kcal mol}^{-1}$) for $\text{LiOH}/\text{H}_2\text{O}$ and $\text{NaOH}/\text{H}_2\text{O}$ solutions can be explained in terms of strong Coulombic interactions between the two cations and the phenolate moieties as well as in terms of electrostatic interactions between the cations and the six phenyl rings. To obtain more information about the interaction between the cesium (or thallium) cation and host **1**, the optimized geometries of the two complexes have been determined from DFT calculations (Supporting Information, Figure 26),

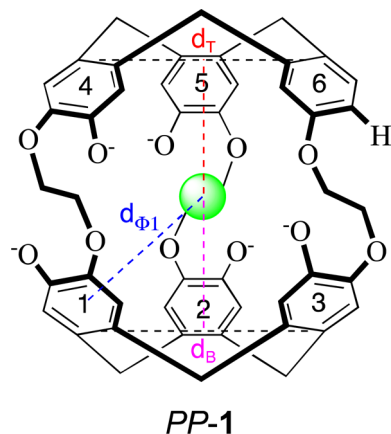
Table 3. Distances (in Å) of the Cs⁺ and Tl⁺ Cations with Respect to the Six Phenyl Rings (d_{Φ_1} to d_{Φ_6}) and to the Two Average Plane of the Caps (d_T to d_B), Determined from the Optimized Geometries of the Cs⁺@PP-1 and Tl⁺@PP-1 Complexes, Considering the GTT Conformation of the Linkers^a

complex	d_{Φ_1}	d_{Φ_2}	d_{Φ_3}	d_{Φ_4}	d_{Φ_5}	d_{Φ_6}	d_T	d_B
Cs ⁺ @PP-1	4.082	4.042	3.323	4.765	4.096	3.916	4.048	3.584
Tl ⁺ @PP-1	3.504	3.424	2.830	5.494	4.742	4.737	4.923	2.661

^aThe numbering of the six phenyl rings and the identification of the distances are given in Scheme 2.

considering the GTT conformation of the linkers. The distances of the two cations with respect to the six phenyl rings and to the average plane of the two caps are reported in Table 3. It is clear that the two cations are closer to the phenyl ring, facing the phenyl ring bearing the hydrogen atom. More globally, the two cations are closer to the CTB unit bearing the three phenolate groups and therefore the highest electronic density. This excentered position of the cation is more pronounced for the thallium and is certainly related to the stronger spectral modifications of the ECD spectra observed for the Tl⁺@PP-1 complex, especially in the ¹L_b region (above 280 nm).

Scheme 2. Numbering of the Six Phenyl Rings and Identification of the Distances d_{Φ_1} , d_T , and d_B



This study, and that reported recently,³ show that host **1** binds alkali cations in the order Tl⁺ > Cs⁺ >> Rb⁺ >> K⁺ > Na⁺, Li⁺ suggesting that the greater the polarizability of the cations, the larger the stability of the complexes. The high affinity of host **1** for Tl⁺ has been also confirmed for the first time by ²⁰⁵Tl NMR spectroscopy. The huge chemical shift (δ = 886 ppm) observed between the unbound thallium cation in solution and Tl⁺ encapsulated in host **1** is unprecedented. This NMR result reflects the very specific interaction of the thallium cation with the cavity of cryptophane **1**. It is also remarkable that, even at 353 K, the NMR signal corresponding to the ²⁰⁵Tl⁺@PP-1 complex is still clearly visible.

Selectivity of PP-1. This study shows that the binding process of Cs⁺ and Tl⁺ by host **1** is very efficient even in the presence of a large excess of Li⁺, Na⁺, and K⁺ cations. For instance, in LiOH/H₂O (0.1 M) and NaOH/H₂O (0.1 M) solutions, very high binding constants have been measured at 298 K for Cs⁺@PP-1 and Tl⁺@PP-1 complexes (see Table 1). Binding constants lower by 1 order of magnitude have been measured in KOH/H₂O (0.1 M) solution. These results show the very high selectivity of Cs⁺ and Tl⁺ cations toward Li⁺, Na⁺, and even K⁺. Additional experiments performed in LiOH/H₂O solution at higher LiOH concentration (1 M) still reveal the efficient binding of Cs⁺ and Tl⁺ cations by host **1** under these

conditions, and binding constants as high as $K = 9.3 \times 10^6 \text{ M}^{-1}$ and $7.0 \times 10^7 \text{ M}^{-1}$ have been measured for Cs⁺ and Tl⁺, respectively. The strong affinity of **1** for these two cations is also confirmed by ECD experiments performed in LiOH/H₂O (1 M), NaOH/H₂O (1 M), and KOH/H₂O (1 M) solutions, which show significant changes of the ECD spectrum of PP-1 upon the addition of a very small amount of Cs⁺ and Tl⁺ cations (see Supporting Information, Figures 4 and 15). Nevertheless, in KOH solution, a competition between Tl⁺ (or Cs⁺) and the potassium cations present in the solution occurs since spectral changes in the ECD spectra of PP-1 are still observed upon the addition of more than one equivalent of guest. A similar effect occurs in LiOH (1 M) when increasing the temperature (see Supporting Information, Figures 4c). Finally, spectral modification of the ECD spectrum of free guest PP-1 still occurs when Cs⁺ and Tl⁺ cations are added to a solution containing a mixture of LiOH (1 M), NaOH (1 M), and KOH (1 M). This last experiment shows that host **1** can be used under extreme basic conditions, revealing the very high selectivity of PP-1 for the thallium and the cesium cations.

CONCLUSIONS

The binding properties of thallium and cesium cations by the enantiopure cryptophane PP-1 have been thoroughly investigated in water under basic condition. Host **1** shows a very strong affinity for both the cesium and thallium cations in a large range of experimental conditions (nature, concentration of the counterion of the solution, and temperature). The high affinity of cryptophane **1** for Cs⁺ and Tl⁺ cations is preserved at higher counterion concentration and under extreme basic conditions, revealing the stability and the great selectivity of this supramolecular system toward Li⁺, Na⁺, and K⁺ cations. The binding process has been easily evidenced by ECD spectroscopy, which reveals strong modifications of the ECD spectrum of the guest free PP-1, in the 220–380 nm region, upon encapsulation of the two cations. These spectral modifications reflect the conformational changes of the three linkers of the cryptophane, required to maximize the host–guest interactions. Our results show that the binding process is more efficient at low LiOH concentration (i.e., < 0.1 M) for which host **1** favors the *gauche* conformations of the linkers, generating a cavity size already well adapted for the encapsulation of Cs⁺ and Tl⁺ cations. At higher LiOH concentration, the guest free host **1** exhibits an all-*trans* conformation of the linkers leading to a larger cavity size, which is less favorable to the interaction with these two cations.

The thallium cation exhibits a higher affinity with PP-1 than the cesium cation since the binding constants determined from ITC experiments for the Tl⁺@PP-1 complex were found approximately 1 order of magnitude greater than those measured for the Cs⁺@PP-1 complex, under the same experimental conditions. The large polarizability of Tl⁺, which is about twice that of Cs⁺, can explain this result. The encapsulation of thallium by host **1** has been characterized for

the first time by a strongly high-field shifted ^{205}Tl NMR signal (886 ppm), revealing the very specific interaction of the thallium cation with the cavity of cryptophane **1**. In contrast to what is observed for the complexation of neutral molecules by cryptophanes, the guest/host molecular volume ratio is not the preponderant factor in the binding process. Instead, the Coulombic interactions between TI^+ (or Cs^+) and phenolate moieties as well as electrostatic interactions between cationic species and π -donor cavity of the hosts are responsible for this very good binding.

All combined together, our results show that host **1** is probably one of the most efficient organic systems ever synthesized for encapsulating cesium or thallium cations in water. These encouraging results warrant further investigations. For instance, we can modify the length of the linkers (size of the cavity) and/or the substituents attached on the phenyl rings (electronic density) to improve both the affinity and the selectivity of the host for these two cations. In addition, the synthesis of cryptophanes soluble in aqueous solutions at neutral pH would be suitable for a better understanding of the host–guest interactions required to observe cesium or thallium complexation with cryptophane derivatives. Moreover, the functionalization and the grafting of these molecular sensors onto solid substrates, and in particular onto superparamagnetic nanoparticles, can be envisaged. It will be an important step forward in the development of new materials for the selective extraction of cesium (or thallium) in contaminated water.

■ ASSOCIATED CONTENT

■ Supporting Information

ECD spectra recorded at 293 K of *PP-1* in $\text{LiOH}/\text{H}_2\text{O}$, $\text{NaOH}/\text{H}_2\text{O}$, and $\text{KOH}/\text{H}_2\text{O}$ solutions in the presence of different amounts of cesium acetate, cesium hydroxide, cesium carbonate, thallium acetate, and thallium nitrate solutions. ECD spectra of *PP-1* in $\text{LiOH}/\text{H}_2\text{O}$ solution, at different concentration of LiOH , in the presence of different amounts of cesium hydroxide and thallium acetate solutions. ECD spectra of *PP-1*, recorded at different temperatures, in $\text{LiOH}/\text{H}_2\text{O}$ (0.1 M) solution in the presence of different amounts of cesium hydroxide solution. Calorimetric titration of *PP-1* at 298 K in $\text{LiOH}/\text{H}_2\text{O}$, $\text{NaOH}/\text{H}_2\text{O}$, and $\text{KOH}/\text{H}_2\text{O}$ solutions with cesium hydroxide and thallium acetate solutions. Calorimetric titration of *PP-1* at 298 K in $\text{LiOH}/\text{H}_2\text{O}$ solution, at different concentration of LiOH , with cesium hydroxide and thallium acetate solutions. ^{205}Tl NMR spectrum recorded at 353 K of *PP-1* in $\text{NaOD}/\text{D}_2\text{O}$ (0.1 M) solution in the presence of a small amount of thallium acetate. IR spectra of empty *PP-1* as well as $\text{CDCl}_3@PP-1$ and $\text{Cs}^+@PP-1$ complexes in $\text{NaOD}/\text{D}_2\text{O}$ solution (0.21 M). Calculated IR spectra at the B3PW91/6-31G* levels of empty *PP-1* for *GGG*, *GTT*, and *TTT* conformations of the linkers. Optimized geometries of $\text{Cs}^+@PP-1$ and $\text{TI}^+@PP-1$ complexes determined from DFT calculations. Full list of authors for ref 9. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS USED

BaF_2 , barium fluoride; CaF_2 , calcium fluoride; CdSe , cadmium selenide; CsOAc , cesium acetate; Cs_2CO_3 , cesium carbonate; CsOH , cesium hydroxide; CTB, cyclotribenzylene; DFT, density functional theory; ECD, electronic circular dichroism; FTIR, Fourier transform infrared; IR, infrared; ITC, isothermal titration calorimetry; MD, molecular dynamics; NMR, nuclear magnetic resonance; TIOAc, thallium acetate; TlNO_3 , thallium nitrate; VCD, vibrational circular dichroism

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