Supporting Information

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

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S1 : a) ECD spectra recorded at 293 K of PP-1 ([host] = 1.48 10^{-5} M, path length of 1.0 cm) in LiOH/H_2O (0.1 M) solution in presence of different amounts of a cesium acetate solution. b) ECD spectra recorded at 293 K of PP-1 ([host] = 1.48 10^{-5} M, path length of 1.0 cm) in LiOH/H_2O (0.1 M) solution in presence of different amounts of a cesium carbonate solution. In both cases, ECD spectra for higher [Cs^+] are identical to that recorded for 1 eq. of Cs^+.

S2 : ECD spectra recorded at 293 K of PP-1 ([host] from 0.70 to 8.31 10^{-5} M, path length of 0.2 cm or 1.0 cm) in LiOH/H_2O solutions in presence of different amounts of cesium hydroxide. The concentrations of LiOH/H_2O solutions were (a) 0.001 M, (b) 0.0025 M, (c) 0.1 M, (d) 0.5 M and (e) 1 M.

S3 : ECD spectra recorded at 293 K of PP-1 ([host] = 1.04 10^{-5} M, path length of 1.0 cm) in NaOH/H_2O (0.1 M) solution in presence of different amounts of a cesium hydroxide solution. ECD spectra for higher [Cs^+] are identical to that recorded for 1 eq. of Cs^+.

S4 : ECD spectra recorded at (a) 278 K, (b) 293 K and (c) 343 K of PP-1 ([host] from 1.12 to 1.18 10^{-5} M, path length of 1.0 cm) in LiOH/H_2O (1 M) solution in presence of different amounts of a cesium hydroxide solution.
S5 : Calorimetric titration of \( PP-1 \) in \( \text{LiOH/}H_2\text{O} \) (top, left), \( \text{NaOH/}H_2\text{O} \) (top, right), and \( \text{KOH/}H_2\text{O} \) (bottom) solutions (0.1 M). The host solution (top left: \( c=98.4 \) µM; top right: \( c=98.6 \) µM; bottom: \( c=100 \) µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of \( \text{RbCl} \) solution (top left: \( c=995 \) µM; top right: \( c=994 \) µM; bottom: \( c=1.00 \) mM) were added at 3 min intervals.

S6 : Calorimetric titration of \( PP-1 \) in \( \text{LiOH/}H_2\text{O} \) (0.1 M) solution in presence of \( \text{RbCl} \) (left: \( c=300 \) µM; right: \( c=301 \) µM). The host solution (left: \( c=29.9 \) µM; right: \( c=30.2 \) µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of \( \text{CsOH/}H_2\text{O} \) solution (left: \( c=402 \) µM; right: \( c=399 \) µM) were added at 3 min intervals.

S7 : Calorimetric titration of \( PP-1 \) in \( \text{NaOH/}H_2\text{O} \) (0.1 M) solution in presence of \( \text{RbCl} \) (left: \( c=299 \) µM; right: \( c=299 \) µM). The host solution (left: \( c=30.1 \) µM; right: \( c=29.9 \) µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of \( \text{CsOH/}H_2\text{O} \) solution (left: \( c=398 \) µM; right: \( c=403 \) µM) were added at 3 min intervals.

S8 : Calorimetric titration of \( PP-1 \) in \( \text{KOH/}H_2\text{O} \) (0.1 M) solution in presence of \( \text{RbCl} \) (left: \( c=300 \) µM; right: \( c=308 \) µM). The host solution (left: \( c=30.0 \) µM; right: \( c=30.0 \) µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of \( \text{CsOH/}H_2\text{O} \) solution (left: \( c=399 \) µM; right: \( c=400 \) µM) were added at 3 min intervals.

S9 : Calorimetric titration of \( PP-1 \) in \( \text{LiOH/}H_2\text{O} \) (0.0025 M) solution in presence of \( \text{RbCl} \) (left: \( c=301 \) µM; right: \( c=300 \) µM). The host solution (left: \( c=30.1 \) µM; right: \( c=29.9 \) µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of \( \text{CsOH/}H_2\text{O} \) solution (left: \( c=397 \) µM; right: \( c=404 \) µM) were added at 3 min intervals.

S10 : Calorimetric titration of \( PP-1 \) in \( \text{LiOH/}H_2\text{O} \) (0.02 M) solution in presence of \( \text{RbCl} \) (301 µM). The host solution (29.8 µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of \( \text{CsOH/}H_2\text{O} \) solution (401 µM) were added at 3 min intervals.

S11 : Calorimetric titration of \( PP-1 \) in \( \text{LiOH/}H_2\text{O} \) (0.5 M) solution in presence of \( \text{RbCl} \) (c=299 µM). The host solution (c=30.2 µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of \( \text{CsOH/}H_2\text{O} \) solution (c=400 µM) were added at 3 min intervals.

S12 : Calorimetric titration of \( PP-1 \) in \( \text{LiOH/}H_2\text{O} \) (1 M). The host solution (left: \( c=100 \) µM; right: \( c=80.0 \) µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of \( \text{CsOH/}H_2\text{O} \) solution (c=997 µM; c=1.012 mM) were added at 3 min intervals.
S13: ECD spectra recorded at 293 K of PP-1 ([host] = 1.15 $10^{-5}$ M, path length of 1.0 cm) in LiOH/H$_2$O (0.1 M) solution in presence of different amounts of a thallium nitrate solution. ECD spectra for higher [Tl$^+$] are identical to that recorded for 1 eq. of Tl$^+$. 

S14: ECD spectra recorded at 293 K of PP-1 ([host] from 1.08 to 1.34 $10^{-5}$ M, path length of 1.0 cm) in LiOH/H$_2$O solutions in presence of different amounts of thallium acetate. The concentrations of LiOH/H$_2$O solutions were (a) 0.001 M, (b) 0.1 M, and (c) 1 M.

S15: ECD spectra recorded at 293 K of PP-1 ([host] from 1.08 to 1.19 $10^{-5}$ M, path length of 1.0 cm) in (a) LiOH/H$_2$O (1 M), (b) NaOH/H$_2$O (1 M), and (c) KOH/H$_2$O (1 M) solutions in presence of different amounts of a thallium nitrate solution.

S16: ECD spectra recorded at 293 K of PP-1 ([host] = 1.39 $10^{-5}$ M, path length of 1.0 cm) in LiOH/H$_2$O (1 M) + NaOH/H$_2$O (1 M) + KOH/H$_2$O (1 M) solution in presence of different amounts of a thallium nitrate solution.

S17: Calorimetric titration of PP-1 in LiOH/H$_2$O (0.1 M) solution in presence of RbCl (left: c=301 µM; right: c=299 µM). The host solution (left: c=30.2 µM; right: c=29.9 µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of TIOAc/H$_2$O solution (left: c=402 µM; right: c=401 µM) were added at 3 min intervals.

S18: Calorimetric titration of PP-1 in NaOH/H$_2$O (0.1 M) solution in presence of RbCl (left: c=298 µM; right: c=300 µM). The host solution (left: c=30.0 µM; right: c=29.8 µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of TIOAc/H$_2$O solution (left: c=400 µM; right: c=399 µM) were added at 3 min intervals.

S19: Calorimetric titration of PP-1 in KOH/H$_2$O (0.1 M) solution in presence of RbCl (c=300 µM). The host solution (c=30.0 µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of TIOAc/H$_2$O solution (c=402 µM) were added at 3 min intervals.

S20: Calorimetric titration of PP-1 in LiOH/H$_2$O (0.0025 M) solution in presence of RbCl (left: c=299 µM; right: c=298 µM). The host solution (left: c=30.1 µM; right: c=30.0 µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of TIOAc/H$_2$O solution (left: c=398 µM; right: c=400 µM) were added at 3 min intervals.

S21: Calorimetric titration of PP-1 in LiOH/H$_2$O (0.02 M) solution in presence of RbCl (300 µM). The host solution (30.1 µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of TIOAc/H$_2$O solution (401 µM) were added at 3 min intervals.

S22: Calorimetric titration of PP-1 in LiOH/H$_2$O (0.5 M) solution in presence of RbCl (c=299 µM). The host solution (c=30.2 µM) was placed into the calorimeter cell (1.4 mL) and
28 successive aliquots (10 µL) of TIOAc/H₂O solution (c=400 µM) were added at 3 min intervals.

S23 : Calorimetric titration of PP-1 in LiOH/H₂O (1 M). The host solution (left: c=100 µM; right: c=100 µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of TIOAc/H₂O solution (left: c=1.0 mM; right: c=1.0 mM) were added at 3 min intervals.

S24 : ²⁰⁵Tl NMR spectra recorded at various temperatures (between 278 to 353 K) of PP-1 in NaOD/D₂O (0.1 M) solution in presence of a small amount of thallium acetate.

S25 : Experimental IR spectra of empty PP-1 as well as CDCl₃@PP-1 and Cs⁺@PP-1 complexes in NaOD/D₂O solution (0.21 M) reported in (a) the 1420-1350 cm⁻¹ and (b) 1060-970 cm⁻¹ regions. The concentration of host 1 was 0.030 M.

Calculated IR spectra at the B3PW91/6-31G* levels of empty PP-1 for GGG, GTT and TTT conformations of the linkers reported in (c) the 1430-1350 cm⁻¹ and (d) 1060-970 cm⁻¹ regions. For comparison to experiment, the calculated frequencies were scaled by 0.968 and the calculated intensities were converted to Lorentzian bands with a half-width of 7 cm⁻¹.

S26 : Optimized geometries of Cs⁺@PP-1 (top) and Tl⁺@PP-1 (bottom) complexes determined from DFT calculations, considering the GTT conformation of the linkers. The hydrogen atoms have been removed, except the one replacing the hydroxyl function.

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Figure S1: a) ECD spectra recorded at 293 K of PP-1 ([host] = 1.48 \times 10^{-5} \text{ M}, \text{ path length of 1.0 cm}) in LiOH/H_2O (0.1 M) solution in presence of different amounts of a cesium acetate solution. b) ECD spectra recorded at 293 K of PP-1 ([host] = 1.48 \times 10^{-5} \text{ M}, \text{ path length of 1.0 cm}) in LiOH/H_2O (0.1 M) solution in presence of different amounts of a cesium carbonate solution. In both cases, ECD spectra for higher [Cs^+] are identical to that recorded for 1 eq. of Cs^+. 
Figure S2: ECD spectra recorded at 293 K of PP-1 ([host] from 0.70 to 8.31 $10^{-5}$ M, path length of 0.2 cm or 1.0 cm) in LiOH/H$_2$O solutions in presence of different amounts of cesium hydroxide. The concentrations of LiOH/H$_2$O solutions were (a) 0.001 M, (b) 0.0025 M, (c) 0.1 M, (d) 0.5 M and (e) 1 M.
Figure S3: ECD spectra recorded at 293 K of PP-1 ([host] = 1.04 \times 10^{-5} \text{ M}, path length of 1.0 cm) in NaOH/H_2O (0.1 M) solution in presence of different amounts of a cesium hydroxide solution. ECD spectra for higher [Cs\(^+\)] are identical to that recorded for 1 eq. of Cs\(^+\).
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Figure S5: Calorimetric titration of PP-1 in LiOH/H$_2$O (top, left), NaOH/H$_2$O (top, right), and KOH/H$_2$O (bottom) solutions (0.1 M). The host solution (top left: c=98.4 μM; top right: c=98.6 μM; bottom: c=100 μM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 μL) of RbCl solution (top left: c=995 μM; top right: c=994 μM; bottom: c=1.00 mM) were added at 3 min intervals.
Figure S6: Calorimetric titration of PP-1 in LiOH/H$_2$O (0.1 M) solution in presence of RbCl (left: c=300 µM; right: c=301 µM). The host solution (left: c=29.9 µM; right: c=30.2 µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of CsOH/H$_2$O solution (left: c=402 µM; right: c=399 µM) were added at 3 min intervals.
Figure S7: Calorimetric titration of PP-I in NaOH/H₂O (0.1 M) solution in presence of RbCl (left: c=299 µM; right: c=299 µM). The host solution (left: c=30.1 µM; right: c=29.9 µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of CsOH/H₂O solution (left: c=398 µM; right: c=403 µM) were added at 3 min intervals.
Figure S8: Calorimetric titration of PP-1 in KOH/H$_2$O (0.1 M) solution in presence of RbCl (left: c=300 μM; right: c=308 μM). The host solution (left: c=30.0 μM; right: c=30.0 μM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 μL) of CsOH/H$_2$O solution (left: c=399 μM; right: c=400 μM) were added at 3 min intervals.
Figure S9: Calorimetric titration of PP-I in LiOH/H$_2$O (0.0025 M) solution in presence of RbCl (left: c=301 µM; right: c=300 µM). The host solution (left: c=30.1 µM; right: c=29.9 µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of CsOH/H$_2$O solution (left: c=397 µM; right: c=404 µM) were added at 3 min intervals.
Figure S10: Calorimetric titration of PP-I in LiOH/H$_2$O (0.02 M) solution in presence of RbCl (301 µM). The host solution (29.8 µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of CsOH/H$_2$O solution (401 µM) were added at 3 min intervals.
Figure S11: Calorimetric titration of PP-I in LiOH/H$_2$O (0.5 M) solution in presence of RbCl (c= 299 µM). The host solution (c=30.2 µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of CsOH/H$_2$O solution (c=400 µM) were added at 3 min intervals.
Figure S12: Calorimetric titration of PP-I in LiOH/H₂O (1 M). The host solution (left: c=100 µM; right: c=80.0 µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of CsOH/H₂O solution (c=997 µM; c=1.012 mM) were added at 3 min intervals.
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Figure S19: Calorimetric titration of PP-I in KOH/H₂O (0.1 M) solution in presence of RbCl (c= 300 µM). The host solution (c=30.0 µM) was placed into the calorimeter cell (1.4 mL) and 28 successive aliquots (10 µL) of TlOAc/H₂O solution (c=402 µM) were added at 3 min intervals.
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Figure S24: $^{205}$Tl NMR spectra recorded at various temperatures (between 278 to 353 K) of $PP$-1 in NaOD/D$_2$O (0.1 M) solution in presence of a small amount of thallium acetate.
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S25 : Optimized geometries of Cs$^+$@PP-1 (top) and Tl$^+$@PP-1 (bottom) complexes determined from DFT calculations, considering the GTT conformation of the linkers. The hydrogen atoms have been removed, except the one replacing the hydroxyl function.
Full list of authors of reference [9]