Electronic Supporting Information

Selective inclusion of PO₄³⁻ within persistent dimeric capsules of a tris(thiourea) receptor and evidence of cation/solvent sealed unimolecular capsules

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Characterization of receptor L:

Figure S1. $^1$H NMR spectrum of L in DMSO-$d_6$ at 298 K.

Figure S2. $^{13}$C NMR spectrum of L in DMSO-$d_6$ at 298 K.

Figure S3. FT-IR spectrum of receptor L recorded in KBr pellet.
Characterization of HPO$_4^{2-}$-complex, [2(\textit{HL})$^{+}$HPO$_4^{2-}$]$^{-}$3H$_2$O (1a):

**Figure S4.** $^1$H NMR spectrum of complex 1a in DMSO-$d_6$ at 298 K.

**Figure S5.** $^{31}$P NMR spectrum of complex 1a in DMSO-$d_6$ at 298 K.

**Figure S6.** FT-IR spectrum of complex 1a recorded in KBr pellet.
Characterization of $\text{PO}_4^{3-}$–encapsulated complex, $3\text{TBA}^+ [2\text{L}(\text{PO}_4^{3-})] 2\text{MeCN}$ (1):

Figure S7. $^1\text{H}$ NMR spectrum of complex 1 in DMSO-$d_6$ at 298 K.

Figure S8. $^{31}\text{P}$ NMR spectrum of complex 1 in DMSO-$d_6$ at 298 K.

Figure S9. FT-IR spectrum of complex 1 recorded in KBr pellet.
Figure S10. Powder XRD patterns of complex 1 recorded with dried crystalline powders.

Characterization of PO$_4^{3-}$-encapsulated complex, 3TEA$^+ [2L(PO$_4^{3-}$)] (1b):

Figure S11. $^1$H NMR spectrum of complex 1b in DMSO-$d_6$ at 298 K.
Figure S12. $^{31}$P NMR spectrum of complex 1b in DMSO-$d_6$ at 298 K.

Figure S13. FT-IR spectrum of complex 1b recorded in KBr pellet.
Figure S14. Powder XRD patterns of complex 1b recorded with dried crystalline powders.
Figure S15. 2D-NOESY NMR spectrum of complex 1b in DMSO-\textit{d}_6 at 298 K.
Figure S16. Partial (aromatic region) 2D-NOESY NMR spectrum of complex 1b in DMSO-\textit{d}_{6} at 298 K, in presence of 0.5 equivalent 2:1 mixture of TBA(OH) and TBA(H_{2}PO_{4}).
Characterization of $\text{F}^-$-encapsulated complex, $\text{TBA}^+[(\text{I}((\text{F})/\text{DMSO}) (2\text{a})$:

**Figure S17.** $^1\text{H}$ NMR spectrum of complex $2\text{a}$ in DMSO-$d_6$ at 298 K.

**Figure S18.** $^{19}\text{F}$ NMR spectrum of complex $2\text{a}$ in DMSO-$d_6$ at 298 K.

**Figure S19.** FT-IR spectrum of complex $2\text{a}$ recorded in KBr pellet.
Characterization of $\text{CO}_3^{2-}$–encapsulated complex, $2\text{TEA}^+[2L(\text{CO}_3^{2-})]$ (3):

**Figure S20.** $^1\text{H}$ NMR spectrum of complex 3 in DMSO-$d_6$ at 298 K.

**Figure S21.** FT-IR spectrum of complex 3 recorded in KBr pellet.
Figure S22. Partial (aromatic region) 2D-NOESY NMR spectrum of complex 3 in DMSO-$d_6$ at 298 K.
Characterization of $\text{SO}_4^{2-}$–encapsulated complex, $\text{2TBA}^+[L(\text{SO}_4^{2-})] \tag{4}$:

**Figure S23.** $^1\text{H}$ NMR spectrum of complex 4 in DMSO-$d_6$ at 298 K.

**Figure S24.** FT-IR spectrum of complex 4 recorded in KBr pellet.
Figure S25. 2D-NOESY NMR spectrum of complex 4 in DMSO-$d_6$ at 298 K.
Characterization of Cl⁻-complex, [(HL)*Cl]·DMF (5):

**Figure S26.** ¹H NMR spectrum of complex 5 in DMSO-d₆ at 298 K.

**Figure S27.** FT-IR spectrum of complex 5 recorded in KBr pellet.
Figure S28. Expanded $^1$H NMR spectra of 1a obtained upon titration with increasing equivalents of TBAF in DMSO-$d_6$ showing the selective formation of phosphate capsule (1) in solution.
Figure S29. $^1$H NMR spectrum of complex 1a in presence of excess TEA(AcO) in DMSO-$d_6$ showing the selective formation of phosphate capsule (1b) in solution.

Additional Crystallographic data:

Figure 30. Crystal packing diagram of complex 1a (view down the crystallographic c-axis).
Figure 31. Crystal packing diagram of complex 1b, showing the cylindrical voids of 568 Å³ (view down the crystallographic c-axis).

Figure 32. Crystal packing diagram of complex 2a (view down the crystallographic c-axis).
**Figure 33.** Crystal packing diagram of complex 3 (view down the crystallographic c-axis).

**Figure 34.** Crystal packing diagram of complex 4 (view down the crystallographic a-axis).
Figure 35. Crystal packing diagram of complex 5 (view down the crystallographic b-axis).