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Supporting Information

pH-Controlled Molecular Switches and Substrate-Directed Self-Assembly of Molecular Capsules with a Calix[4]pyrrole Derivative.

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X-Ray Crystallography

In the structure of [**1**·*p*-C_6H_4(COOH)(COO^-)($^+NMe_4$)], both of the 1,4-benzenedicarboxylate guest mono-anions were found to be disordered. In each case, two orientations were identified of *ca.* 54:46% and *ca.* 67:33% occupancy for complexes **A** and **B** respectively, with the major occupancy non-hydrogen atoms being refined anisotropically and those of the minor occupancy orientations being refined isotropically. Importantly, the six-membered ring in each orientation was modelled as a perfect hexagon of side length 1.39 Å, and the carboxylic acid units were also optimised. Amongst other constraints, all 16 of the C–O linkages across the four orientations (4 such linkages in each terephthalate anion) were constrained to be the same. As a result of this disorder, and the optimisations and constraints needed to achieve a reasonable model, no carboxylate protons could be located. As the presumed N–H protons of the macrocycles could also not be located, we can only infer where the N–H and O–H protons reside.

The simplest situation would be to consider each of the pyrrole nitrogens of the macrocycles to be protonated, giving a neutral species. The adjacent O(51)/O(52) and O(51')/O(52') carboxylate units would then have to be deprotonated, and to maintain an overall mono-negative charge for each inclusion complex (to balance the one Me_4N mono-cation per complex) the O(60)/O(61) and O(60')/O(61') CO_2 units would have to be protonated. This view is supported by the close intermolecular approaches of these carboxylate units (see Fig. S3). Unfortunately, the disorder present in these anions (*vide supra*) precludes any detailed analysis.

Both of the tetramethylammonium cations were found to be disordered. In each case two orientations were identified [*ca.* 60:40% for the N(70) cation, and *ca.* 66:34% for the N(80) cation] with common positions for the central nitrogen. The nitrogens, and the carbons of the major occupancy orientations, were refined anisotropically, the minor occupancy atoms being refined isotropically.

One 50% occupancy included ethyl acetate solvent molecule was also found to be present in the structure; all the non-hydrogen atoms of this molecule were refined anisotropically. Other scattered electron density peaks were identified, and these were assumed to be part of numerous other partial occupancy solvent molecules. Partial occupancy oxygen and carbon atoms were added at these sites, and the occupancies adjusted to give the number of oxygen and carbon atoms needed for a further 50% occupancy ethyl acetate, making a total of one

solvent molecule per two complexes; these scattered atoms were all of less than 40% occupancy and were all refined isotropically.

Unlike the situation for the structure of [**1**·*p*-$C_6H_4(COOH)(COO^-)(^+NMe_4)$], in the X-ray structure of [2(**1**)·*m*-$C_6H_4(COO^-)_2(^+NMe_4)_2$] all 8 of the N–H protons were easily located from Δ*F* maps, and they were refined subject to an N–H distance constraint of 0.90 Å. The two included acetonitrile molecules in the structure of [2(**1**)·*m*-$C_6H_4(COO^-)_2(^+NMe_4)_2$] were both found to be disordered. In each case three orientations were identified, and all of the non-hydrogen atoms were refined isotropically.

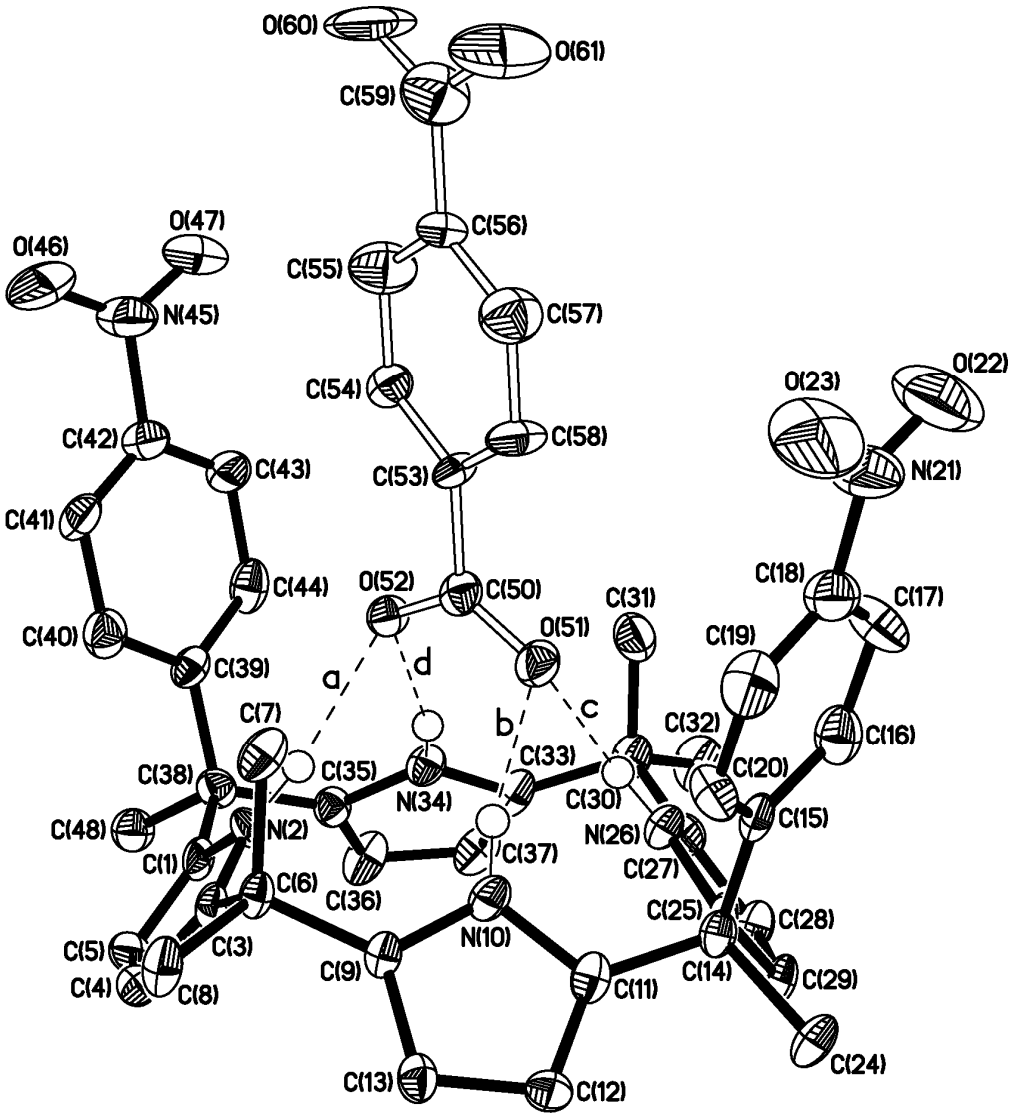

Figure S1. The molecular structure of one of the two crystallographically independent anionic inclusion complexes (**A**) present in the crystals of [**1**·*p*-$C_6H_4(COOH)(COO^-)(^+NMe_4)$] (30% probability ellipsoids).

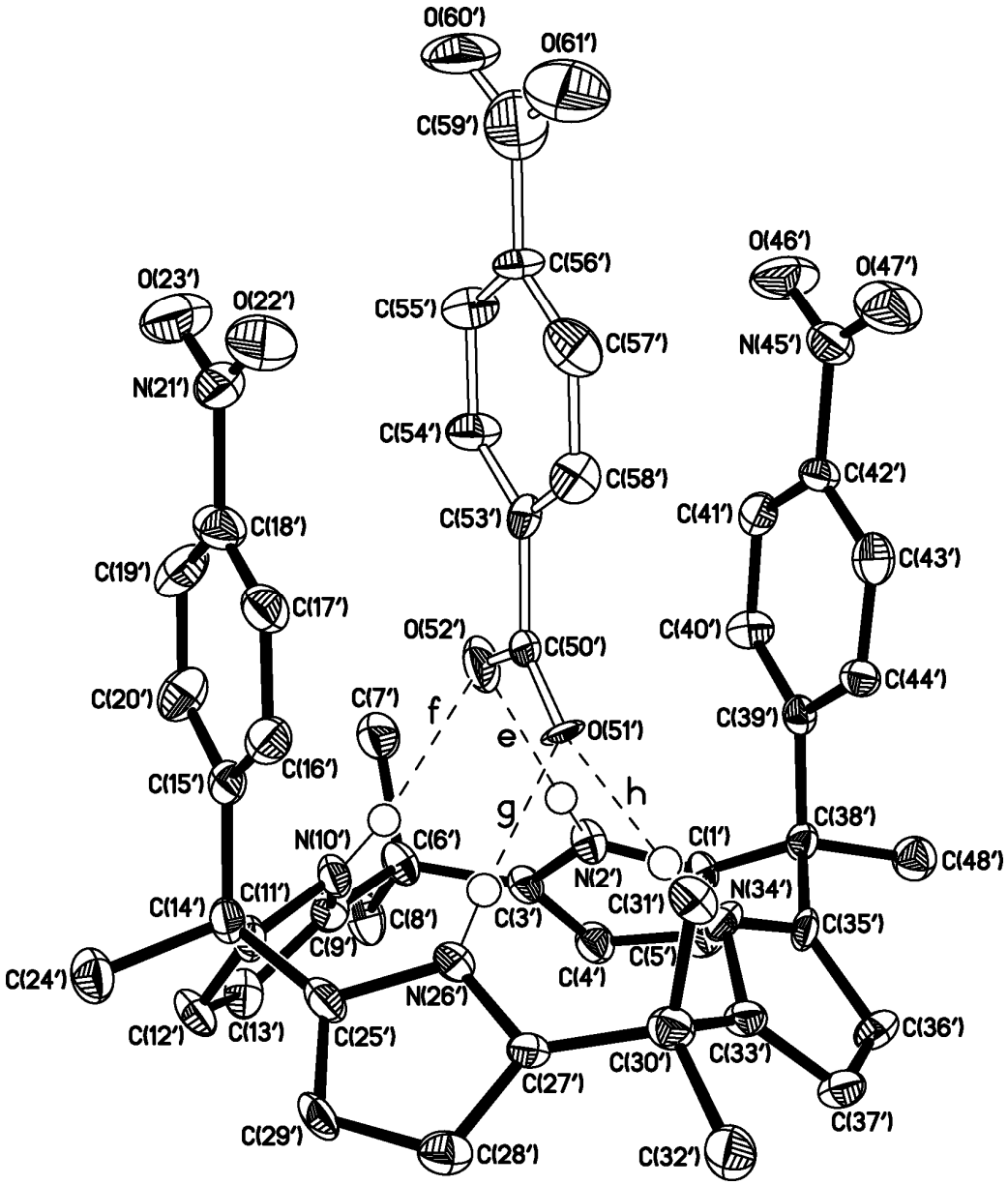

Figure S2. The molecular structure of one of the two crystallographically independent anionic inclusion complexes (**B**) present in the crystals of [**1**·*p*-$C_6H_4(COOH)(COO^-)(^+NMe_4)$] (30% probability ellipsoids).

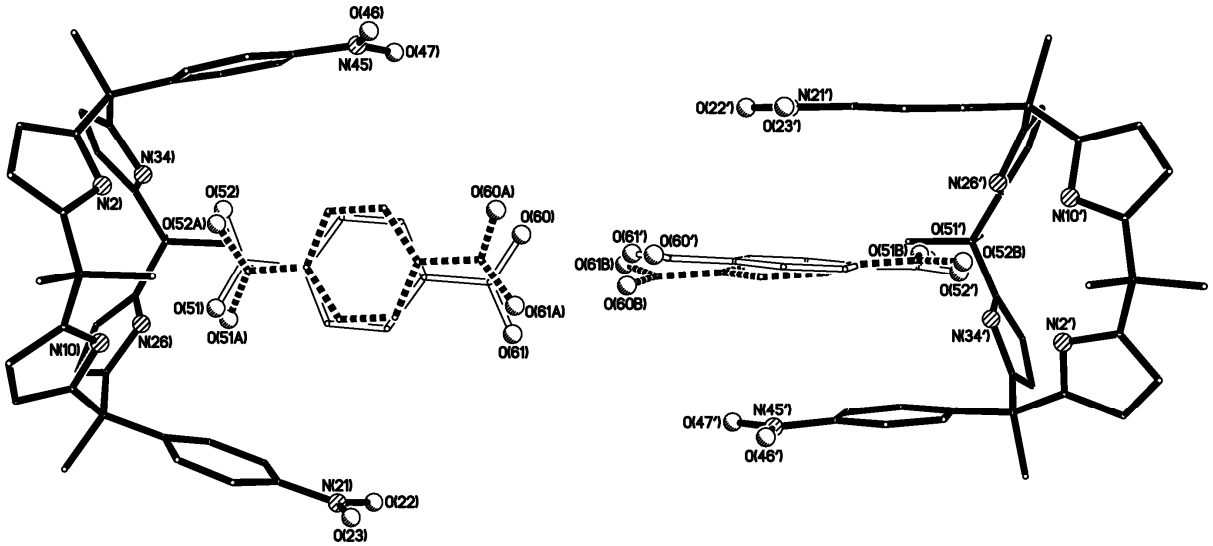

Figure S3. The X-ray molecular structure of [**1**·*p*-$C_6H_4(COOH)(COO^-)(^+NMe_4)$] showing the two crystallographically independent anionic inclusion complexes (**A** to the left, and **B** to the right) and how the protruding ends of the disordered terephthalate anions approach each other. (The major occupancy terephthalate anions are drawn with open bonds, the minor occupancy orientations with dashed bonds).

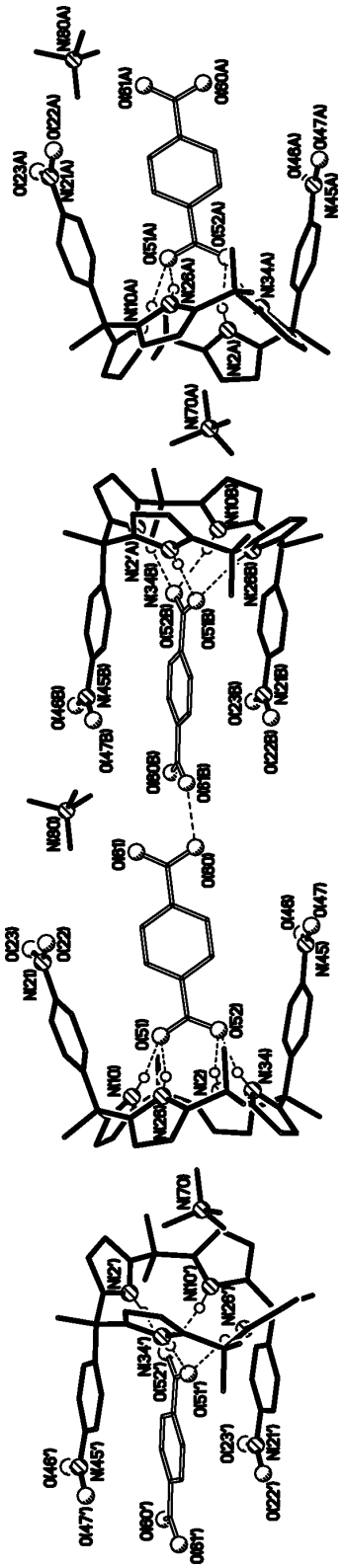

Figure S4. The molecular structure of [**1**·*p*-$C_6H_4(COOH)(COO)^-(^+NMe_4)$] showing the encapsulation of the N(70) NMe_4 cation between two calixpyrrole units [the N(80) NMe_4 cation is not likewise encapsulated].

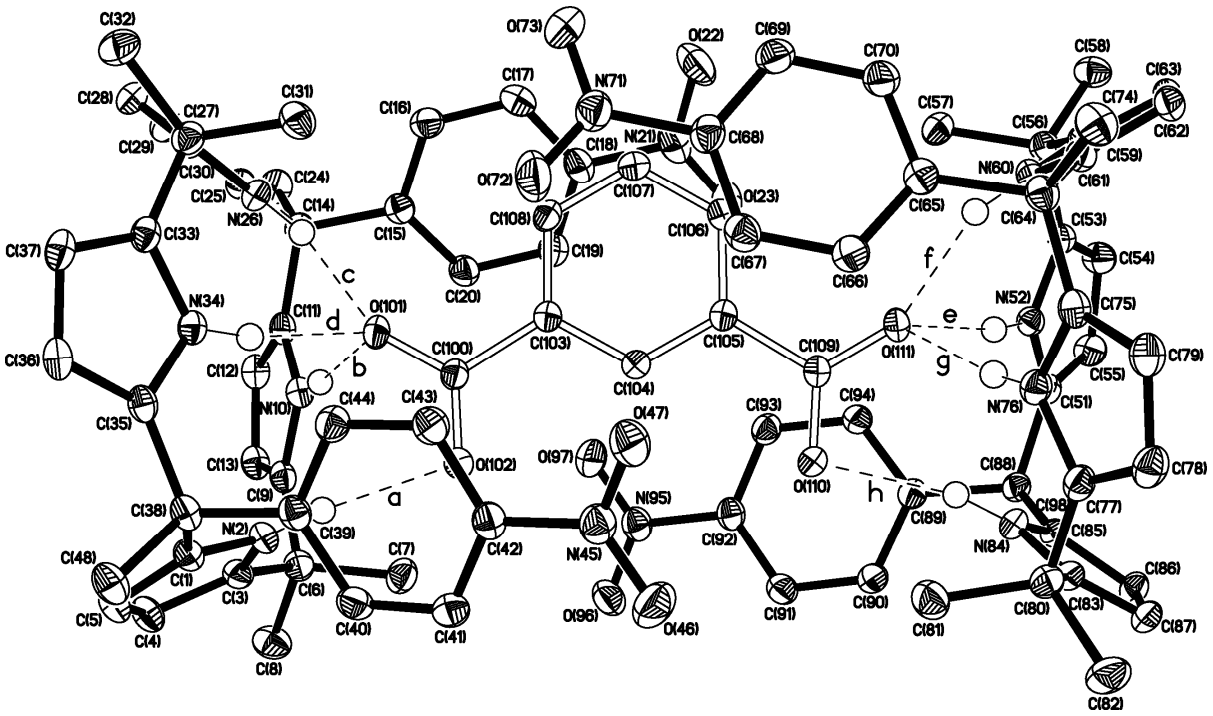

Figure S5. The molecular structure of the dianionic capsular species present in the crystals of [2(**1**)$^{\cdot}$*m*-$C_6H_4(COO^-)_2(^+NMe_4)_2$] (30% probability ellipsoids).

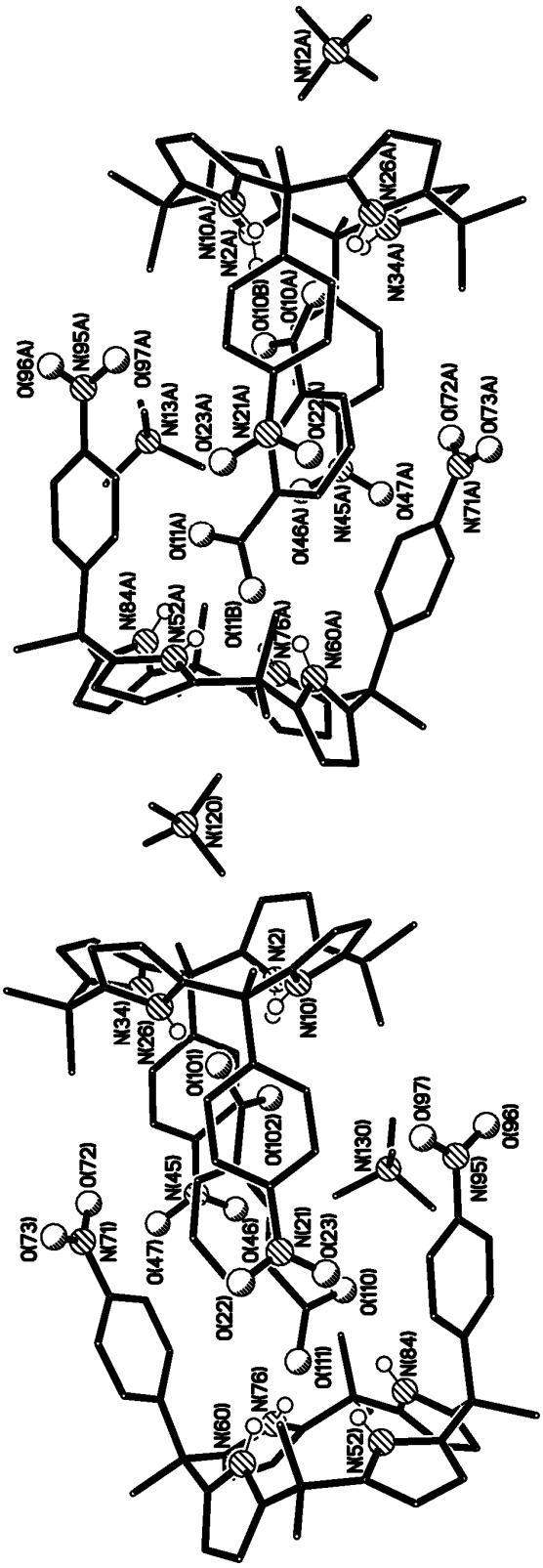

Figure S6. The molecular structure [2(**1**)·*m*-$C_6H_4(COO^-)_2(^+NMe_4)_2$] showing the encapsulation of the N(120) NMe_4 cation between two calixpyrrole units [the N(130) NMe_4 cation is not likewise encapsulated].

Solution Studies

Variable temperature ^{1}H MNR.

Variable temperature ^{1}H MNR experiments were conducted in CD_3CN for mixtures *p*-$C_6H_4(COO^-)_2(^+NnBu_4)_2$ and receptor **1**. For a 1:1 stoichiometry in the range (+25)-(+69) °C (see Figure S10) the proton resonances of the bis-anion coalesced, but did not re-appear as a single resonance. For a 1:2 stoichiometry of salt and receptor respectively, in the range (+25)-(-38) °C the capsule was not observed in a 'frozen' conformation (see Figure S11).

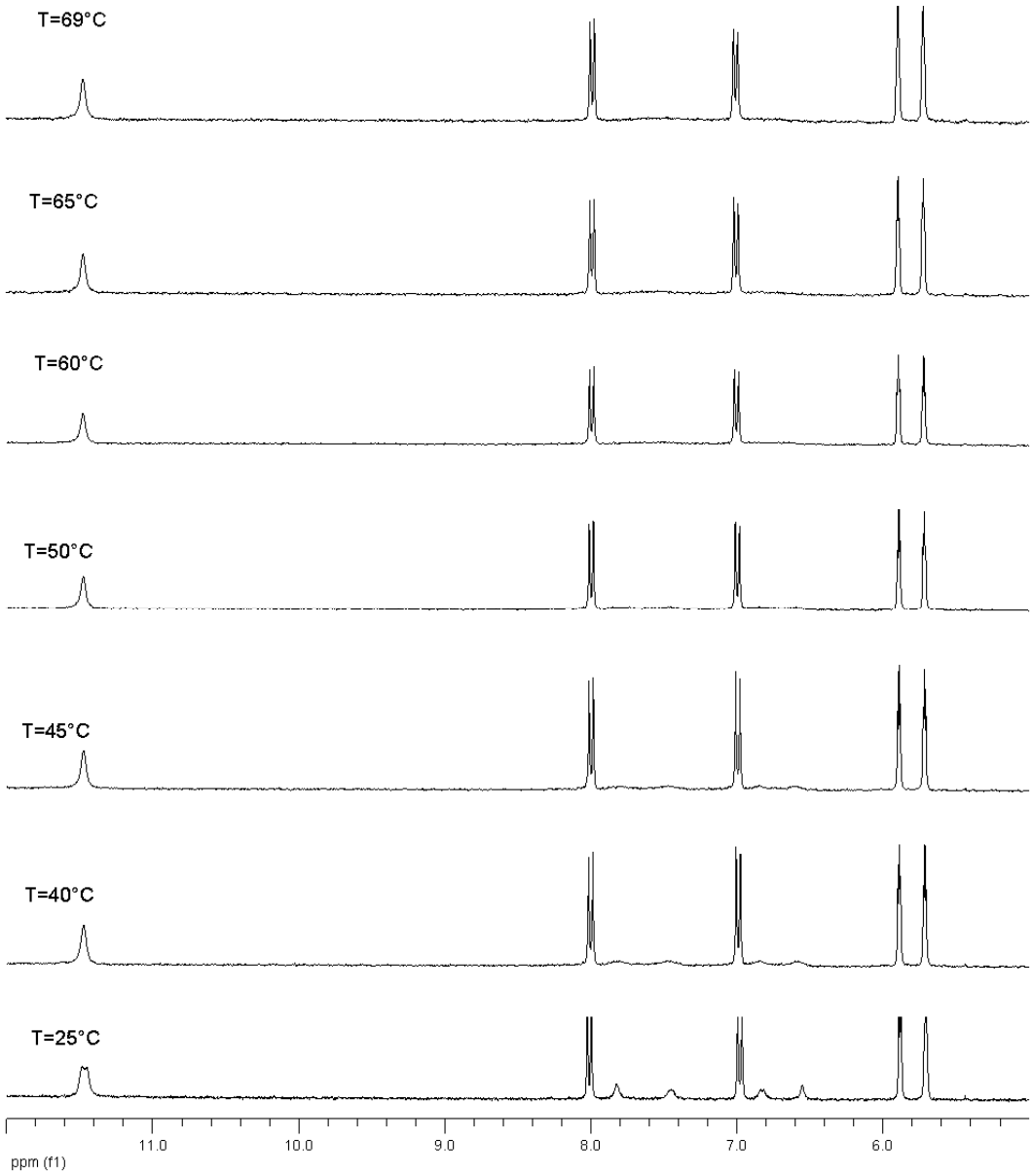

Figure S10. Partial ^{1}H MNR spectra at the indicated temperatures for a 1:1 mixture of $C_6H_4(COO^-)_2(^+NnBu_4)_2$ and receptor **1** in CD_3CN.

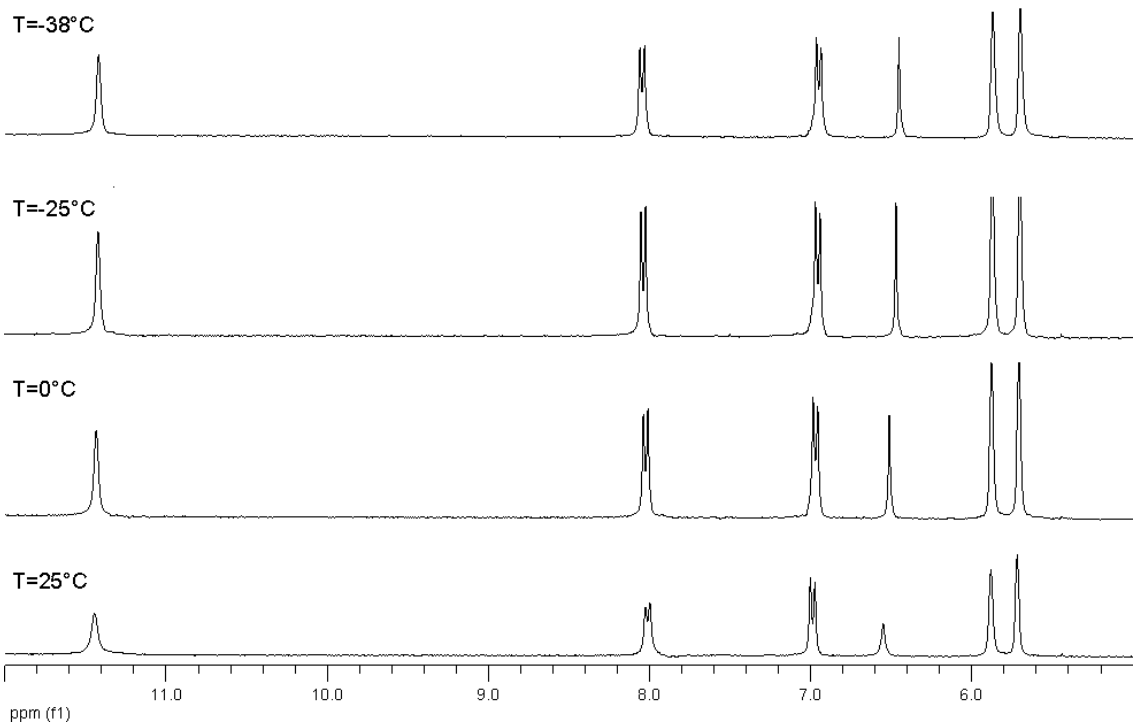

Figure S11. Partial ^{1}H MNR spectra at the indicated temperatures for a 1:2 mixture of $C_6H_4(COO^-)_2(^+NnBu_4)_2$ and receptor **1** respectively in CD_3CN.

Details of the method used to evaluate the ratio between the association constants for the formation of the 1:1 complex of **1** with $[p\text{-}OC_6H_4(COO)]^{2-}(DBUH^+)_2$ and of this latter 1:1 complex with an other unit of the receptor **1**.

We compared the two steps of the binding leading to the molecular caps by ignoring all of the other equilibria that are likely occurring within the multi-component mixture. These include ion-pairings and binding of the calixpyrrole in its cone conformation with cations (interaction with the pyrrole π-units).

With these approximations, and indicating receptor **1** as $C4Py$ and the bis-anion with $A^=$, the two-step assembly of the molecular capsule is described by equations (i) and (ii) for which the $K_{a(1:1)}$ and $K_{a(1:2)}$ can be written.

It can be seen that for the evaluation of $\frac{K_{a(1:1)}}{K_{a(1:2)}}$ it is necessary to measure not only the concentrations of the 1:1 and 1:2 complexes, but also that of the free anion. Since the association constants are both high, it was not possible to observe any free bis-anion until this was added in excess (more than two moles). However, for the same reason, we could assume

that the fraction of free anion derived from the equilibrium was negligible compared to that added in excess. With this latter approximation we measured the relative amounts of 1:1 and of capsular complex in the presence of variable amounts of bis-anions by (^{1}H NMR, appropriate time-dealys were used for reliable integration). Inserting the relevant concentrations in equation (iii) and averaging the results gave the value 0.5 cited in the main text.

i) $C4Py + A^{=} \rightleftarrows C4PyA^{=}$

$$K_{a(1:1)} = \frac{\left[C4PyA^{=}\right]}{\left[C4Py\right]\left[A^{=}\right]}$$

ii) $C4PyA^{=} + C4Py \rightleftarrows C4PyA^{=}C4Py$

$$K_{a(1:2)} = \frac{\left[C4PyA^{=}C4Py\right]}{\left[C4PyA^{=}\right]\left[C4Py\right]}$$

iii) $$\frac{K_{a(1:1)}}{K_{a(1:2)}} = \frac{\left[C4PyA^{=}\right]^2}{\left[C4PyA^{=}C4Py\right]\left[A^{=}\right]}$$