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1. Crystal structure determination of 1A and 1B.

Crystals of 1A and 1B were all of small dimensions and contained a large number of solvent molecules; consequently, to improve the intensity of the diffraction pattern, data collections were carried out using synchrotron radiation at the X-ray diffraction beam-line of the Elettra Synchrotron, Trieste, Italy, employing the rotating-crystal method with the cryo-cooling technique. Routinely, the crystal dipped in Paratone, as cryo-protectant, was mounted in a loop and flash frozen to 100 K with liquid nitrogen. Diffraction data of 1A were indexed and integrated using the XDS package, while MOSFLM was used for 1B. Scaling was carried out with SCALA for datasets collected from crystals of 1A, whereas AIMLESS was used for that one collected from crystals of 1B. The structures were solved by direct methods using SIR2011. Non-hydrogen atoms at full occupancy, or with population equal to or higher than 0.5 were anisotropically refined (H atoms at the calculated positions) with bond length and angle restraints by full-matrix least-squares methods on $F^2$ using SHELXL-14.

The structure of 1A shows disorder in the orientation of a phenyl ring: the two positions were refined at 0.4/0.6 of partial occupancy. Three orientations were identified for an ethyl acetate solvent molecules, refined at 0.4/0.3/0.3 of partial occupancy. A toluene solvent molecule and an ethyl acetate solvent molecule share the same binding site in the calixarene cavity. The two solvent molecules were refined at equal partial occupancy.

Restrains (DFIX, DANG) were applied on bond lengths and angles and thermal parameters (SIMU) for atoms involved in disordered fragments.

The cell contained also a severely disordered solvent molecule with partial occupancy, that was not modelled but taken into account using the SQUEEZE/PLATON procedure. The residual electron density of 37 electrons/cell found in the inner space of the crystal (corresponding to about 6.1% of the cell volume) can be attributed or to 0.7 toluene solvent molecules or to 0.8 ethyl acetate solvent molecules.
Figure S1. Overlay of the crystallographic models of 1A and p-tert-butylcalix[6]arene\textsuperscript{viii} in the pinched conformation.
Figure S2. Diehdral angle between the mean planes calculated for the two sub-cavities in the crystallographic model of 1A.
Figure S3. Three different kinds H-bonds are responsible for the propagation of resorcin[6]arene 1A arrangement along the ac plane. The H-bonds O(2h)···O(3h) and O(5h)···O(6i) give rise to symmetrical rings (defined by the Etter graphs\textsuperscript{1} \textit{R}\textsuperscript{2}(16) and \textit{R}\textsuperscript{2}(24), respectively, whereas the H-bond (O(1h)···O(4h) defines chains of molecule (C(18))).

\textsuperscript{1} M. C. Etter, J. C. MacDonald, J. Bernstein, \textit{Acta Cryst}. (1990), B46, 256-262.
Figure S4. Molecular arrangement of 1A along the ac crystallographic plane.
Calculation of the cavity volume for the capsular assembly 1A₂

The volume of the sub-cavities of the supramolecular capsule 1A₂ was estimated using the VOIDOO software, starting from the crystallographic coordinates of 1A. The following atomic radii were used for the calculations: carbon = 1.70 Å, oxygen = 1.60 Å, nitrogen = 1.65 Å, aliphatic hydrogen = 1.20 Å.

Four molecules of benzene were introduced in the model only at the aim of closing the openings in the capsule walls, so that the virtual probe with radius of 1.4 Å could define the void in the cavity.

The following parameters were changed from their default settings:

- Primary grid spacing: 0.1
- Maximum number of volume-refinement cycles: 30

The average volume of the void space inside the sub-cavity, shown in Figure S5, resulted 252 Å³.

Volumes of toluene and ethyl acetate guests (VG) were also calculated with the same program, and resulted 96 and 85 Å³, respectively.

Figure S5. Surfaces of the voids available in the solid-state structure of the capsule 1A₂.
Figure S6. Dihedral angle between the mean planes calculated for the two sub-cavities in the crystallographic model of 1B.

Table S1.  CH···π interactions between the DMF guest molecules and the aromatic walls of the 1B host. Cg are the center of gravity calculated for the aromatic rings A, B, C, D, E, F (shown in Figure S8).

<table>
<thead>
<tr>
<th>CH···π</th>
<th>Å</th>
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<tbody>
<tr>
<td>C(2sc)···Cg(D)</td>
<td>3.909(3)</td>
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<tr>
<td>C(2sc)···Cg(E)</td>
<td>3.987(2)</td>
</tr>
<tr>
<td>C(1sc)···Cg(C)</td>
<td>3.474(2)</td>
</tr>
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<td>C(2se)···Cg(F)</td>
<td>3.514(2)</td>
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<tr>
<td>C(2se)···Cg(A)</td>
<td>3.692(3)</td>
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<tr>
<td>C(1se)···Cg(B)</td>
<td>3.931(2)</td>
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