Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Diffusion of vaporous guests into a seemingly non-porous organic crystal.

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1. Synthesis of *p-tert*-Butylthiacalix[4]arene

p-tert-Butylthiacalix[4]arene was synthesized according to the method of Patel et al.[1] Tetra methylation of the *p-tert*-butylthiacalix[4]arene was carried out according to the method of Katagiri et al.[2] Purification was achieved by crystallization from hexanes and methanol.

2. Preparation of Single Crystals of 1.

Single crystals of calixarene **1**, were prepared by slow sublimation at 240 °C under a vacuum of 0.5 mm Hg in a Büchi® glass oven.

3. Sorption of Gaseous Guests

Sorption of anhydrous HCl was achieved by placing freshly sublimed single crystals of calixarene **1** in an oven-dried gas-tight sealable glass flask, which was evacuated under reduced pressure and pressurized with HCl gas (99 % purity, 1 bar). The flask was then sealed under pressure. Experiments involving absorption of "wet HCl" vapor were performed by placing the sublimed calixarene in a sealable glass vessel above a solution of concentrated hydrochloric acid such that there was no direct contact between the acidic solution and the sublimed material. Absorption of anhydrous iodine was performed in a gas tight glass flask, using calcium chloride as a desiccant, with no direct contact between the iodine and the calixarene material. Absorption of "wet iodine" vapor was achieved by placing sublimed calixarene and iodine above a solution of distilled water in a sealable vessel with no direct contact between the calixarene, iodine and water.

When analyzing the resulting crystals by single crystal X-ray diffraction, an effort was made to select similarly sized crystals for comparative analysis between the wet and dry conditions. A number of different exposure times were tested without large deviation in guest occupancy; however the structures reported in the main text were exposed to vapors of the guest for 1 week.

4. Crystal structure determination

X-ray intensity data were collected on a Bruker SMART Apex CCD diffractometer at 100 K using graphite monochromated MoKα radiation (λ=0.71073 Å). The temperature of the crystals was controlled using an Oxford Cryostream Cooler. Data reduction was carried out by means of a standard procedure using the Bruker software package SAINT.[3] The absorption correction was based on multiple and symmetry equivalent reflections in the data set by using the SADABS program.[4] The structures were solved by direct methods using the SHELXS-97[5] program and were refined by full matrix least squares on F^2 using the program SHELXL-97[5] through the graphical interface X-Seed,[6] which was also used to generate the figures. Non-hydrogen atoms were refined anisotropically except for those constituting the minor component in the disordered model of $\mathbf{1_{I2}}$ and $\mathbf{1_{I2\cdot H2O}}$ which were refined isotropically. The hydrogen atoms of the macrocycles were placed at calculated positions and refined using riding models, and their isotropic displacement parameters were assigned a value 20% higher than the isotropic equivalent for the atom to which they are attached (for methyl hydrogens this value was increased to 50%). Because of the fractional occupancies of the solvent molecules in $\mathbf{1_{HCl}}$, $\mathbf{1_{HCl*H2O}}$ and $\mathbf{1_{I2\cdot H2O}}$, their H atoms were not located.

Crystal data for $\mathbf{1_{HCl}}$: $C_{88}H_{109.36}Cl_{1.36}O_8S_8$, M_r=1599.81, 0.30x0.15x0.08 mm^3, tetragonal, space group P-42$_1$m (No. 113), a=b=19.378(2), c=12.122(1) Å, V=4551.5(8) Å^3, Z=2, D_c=1.167 g/cm^3, F000=1705, Bruker APEX CCD area-detector, MoKα radiation, λ=0.71073 Å, 2θmax=50.4°, 24247 reflections collected, 4202 unique (R_{int}=0.069). Final GooF=1.069, R1=0.046, wR2=0.119, R indices based on 3557 reflections with I>2σ(I), 301 parameters, 43 restraints, Flack parameter -0.13 (10). Lp and absorption corrections applied, μ=0.29 mm^{-1}.

Crystal data for $\mathbf{1_{HCl*H2O}}$: $C_{88}H_{113.08}Cl_{0.20}O_{8.44}S_8$, M_r=1569.47, 0.40×0.20×0.12 mm^3, tetragonal, space group P-42$_1$m (No. 113), a=b=19.365(2), c=12.119(1) Å, V=4544.7(10) Å^3, Z=2, D_c=1.147 g/cm^3, F000=1680, Bruker APEX CCD area-detector, MoKα radiation, λ=0.71073 Å, 2θ$_{\text{max}}$=55.5°, 28695 reflections collected, 5481 unique (R_{int}=0.057). Final GooF=1.046, R1=0.041, wR2=0.098, R indices based on 4701 reflections with I>2σ(I), 298 parameters, 43 restraints, Flack parameter 0.08 (7). Lp and absorption corrections applied, μ=0.25 mm^{-1}.

Crystal data for $\mathbf{1_{I2}}$: $C_{88}H_{112}O_8S_8I_{0.8}$, M_r=1655.78, 0.22×0.14×0.10 mm^3, tetragonal, space group P-42$_1$m (No. 113), a=b=19.544(3), c=11.924(2) Å, V=4554.4(16) Å^3, Z=2, D_c=1.207 g/cm^3, F000=1748.8, Bruker APEX CCD area-detector, MoKα radiation, λ=0.71073 Å, 2θ$_{\text{max}}$=55.9°, 28876 reflections collected, 5545 unique (R_{int}=0.042). Final GooF=1.054, R1=0.054, wR2=0.154, R indices based on 4914 reflections with I > 2σ(I), 323 parameters, 62 restraints, Flack parameter -0.03 (5). Lp and absorption corrections applied, μ=0.52 mm^{-1}.

Crystal data for $\mathbf{1_{I2\cdot H2O}}$: $C_{88}H_{113}I_{0.8}O_9S_8$, M_r=1672.78, 0.25×0.14×0.08 mm^3, tetragonal, space group P-42$_1$m (No. 113), a=b=19.523(2), c=11.951(1) Å, V=4555.1(10) Å^3, Z=2, D_c=1.220 g/cm^3, F000=1767, Bruker APEX CCD area-detector, MoKα radiation, λ=0.71073 Å,

$2\theta_{max}$=55.6º, 28814 reflections collected, 5509 unique (R_{int}=0.052). Final GooF=1.034, R1=0.061, wR2=0.184, R indices based on 4767 reflections with I>2σ(I), 331 parameters, 58 restraints, Flack parameter 0.02 (7). Lp and absorption corrections applied, μ=0.52 mm^{-1}.

In all investigated crystal structures, the unit cell contains two subtly different (*i.e.* symmetry-independent) calixarene molecules; one occupies -4 site symmetry [Wyckoff notation[7] 2a (molecule $\mathbf{1b_1}$)] and the second occupies 2mm site symmetry [Wyckoff notation[7] 2c (molecule $\mathbf{1b_2}$)]. While the molecule $\mathbf{1b_1}$ is fully ordered, the molecule $\mathbf{1b_2}$ displays disorder within all four *t*-butyl groups in a manner such that the central C atom occupies either *m* site symmetry or is located very close to this site and the three methyl groups placed above and below the plane giving two sets of positions each with site occupancies of 0.5 except for the two *t*-butyl group in $\mathbf{1_{I2}}$ and $\mathbf{1_{I2 \cdot H2O}}$ which were modelled as a three part disorder in a 0.4 to 0.4 to 0.2 ratio.

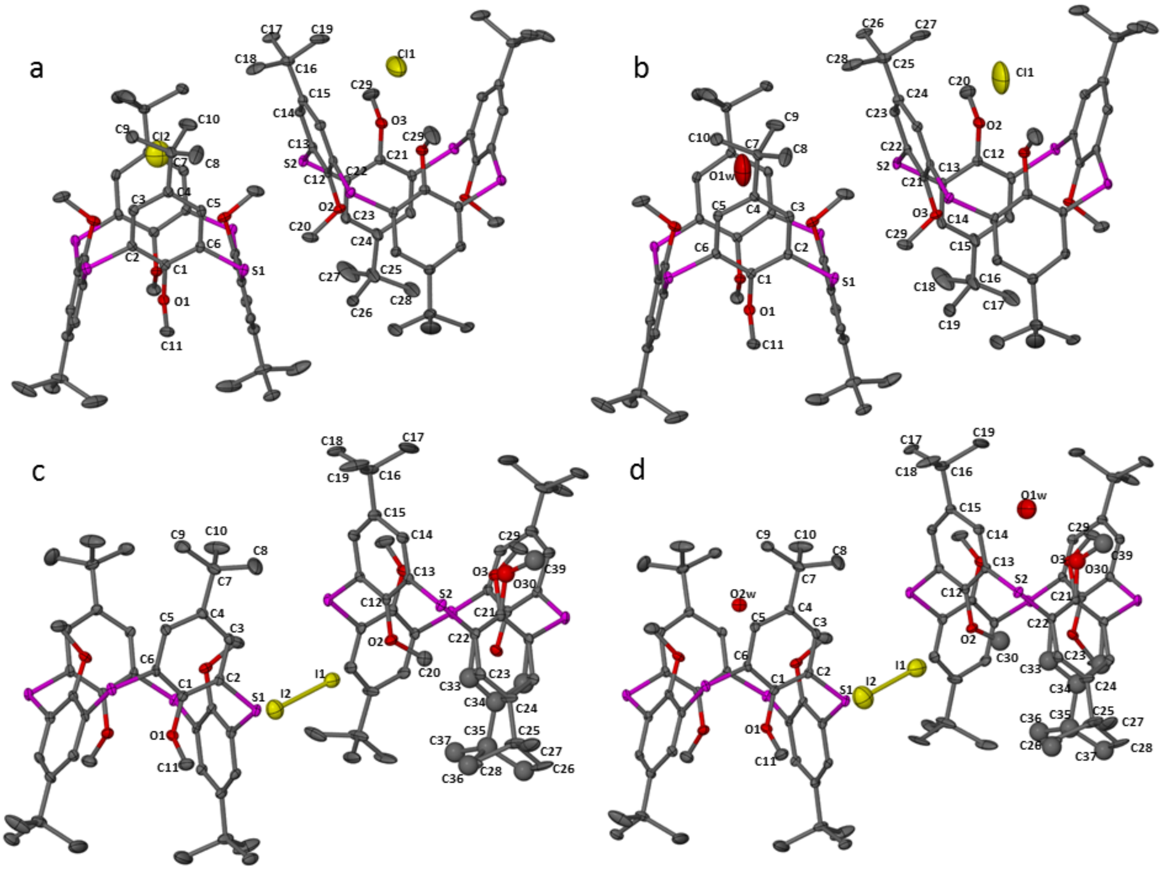

Figure S1. Anisotropic displacement representations for $\mathbf{1_{HCl}}$, $\mathbf{1_{HCl \cdot H2O}}$, $\mathbf{1_{I2}}$ and $\mathbf{1_{I2 \cdot H2O}}$. Labels mark the symmetry independent part of molecules. Displacement ellipsoids are given at 40% probability level. The minor component in $\mathbf{1_{I2}}$ (c) and $\mathbf{1_{I2 \cdot H2O}}$ (d) is shown in ball and stick graphical reperesentation. Symmetry related disorder and all H-atoms have been omitted for clarity.

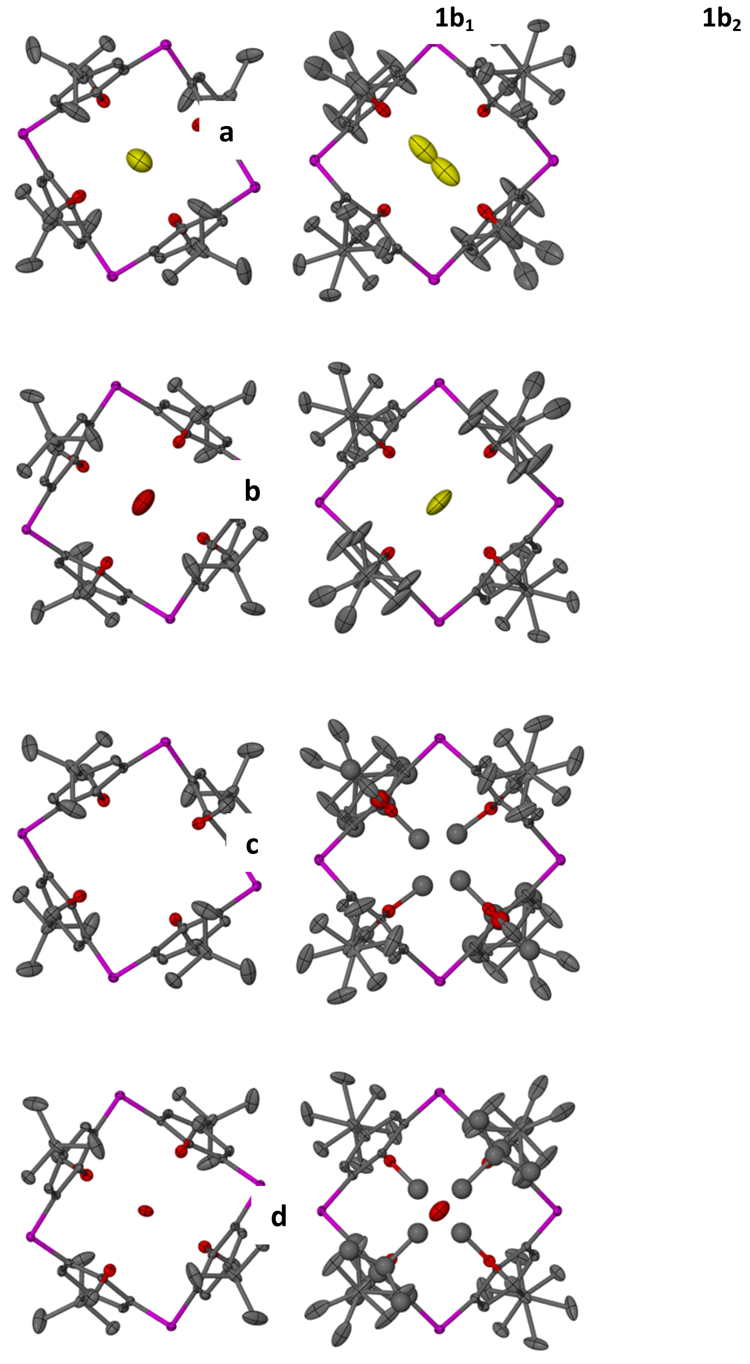

Figure S2. Calixarene molecules in the structures of (a) $\mathbf{1b_{HCl}}$, (b) $\mathbf{1b_{HCl\cdot H2O}}$, (c) $\mathbf{1_{I2}}$ and (d) $\mathbf{1_{I2\cdot H2O}}$ viewed perpendicular to [110]. The *t*-butyl groups of $\mathbf{1b_2}$ are disordered in all crystal structures. The minor component in $\mathbf{1_{I2}}$ and $\mathbf{1_{I2\cdot H2O}}$ is shown in ball and stick graphical reperesentation. All H-atoms have been omitted for clarity.

In the $\mathbf{1_{I2}}$ and $\mathbf{1_{I2\cdot H2O}}$ structures the disordered regions are observed within two of the four aromatic rings and methoxy groups and they are in response to diffusion of the iodine molecules into the crystals. These parts of the molecule were treated as the major and minor components and refined with site occupancy 0.8 and 0.2, respectively. Where necessary, the restraints for the 1,2- and 1,3-distances as well as the ADP restraint (SIMU) and rigid-bond restraint (DELU) were applied.

The positions of solvents (H_2O or HCl) in the endo cavities were determined by analysing the contacts between the highest electron density peaks and the closest oxygen atom of two methoxy groups of calixarene. Based on the results obtained from the CSD[8] we assigned the distance of about 2.9 Å as belonging to a O…O contact while the distance of 3.2 Å corresponded to a Cl…O contact. In the interstitial pockets of $\mathbf{1_{I2}}$ and $\mathbf{1_{I2\cdot H2O}}$ were located two significant peaks of electron density which were modelled as iodine with an I−I bond length of 2.684(3) Å. The presence of the chloride and iodine in the crystals was also confirmed by EDX analysis.

In general the guest molecules occupying the endo voids are placed at special positions on -4 in $\mathbf{1b_1}$ and 2mm in $\mathbf{1b_2}$ site symmetry except for the HCl molecule in $\mathbf{1_{HCl}}$ which is located on one m plane close to 2mm site symmetry and hence is disordered over two equal positions required by the symmetry. The iodine molecule in both structures occupies the special position on mirror plane.

The sites occupancy for solvent molecules (50% of Cl1 and 18% of Cl2 in $\mathbf{1_{HCl}}$, 20% of HCl and 22% of O1w in $\mathbf{1_{HCl\cdot H2O}}$, 20% of I2 in $\mathbf{1_{I2}}$**,** and 20% of I2, 50% of O1w and 25% of O2w in $\mathbf{1_{I2\cdot H2O}}$) were first based on the indications of their atomic thermal factors and then were confirmed by the electron density summation in SQUEEZE routine implemented in Platon.[9] The occupancy of the iodine atoms assigned as 20% in the crystal structure is consistent with the results of EDX analysis of 19.3% calculated over all spectrums.

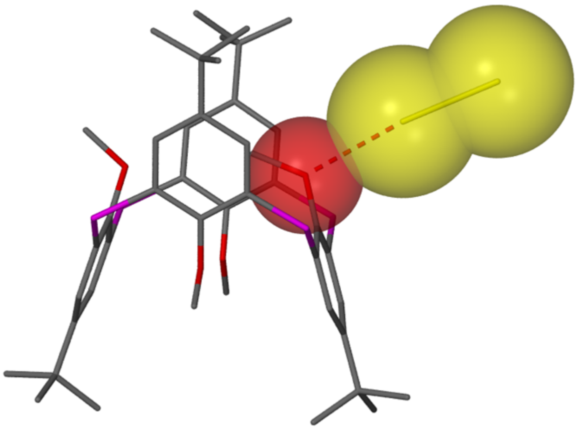

Figure S3. Ilustration of the I I...O intermolecular interactions in $\mathbf{1}_{\mathbf{I2}}$ and $\mathbf{1}_{\mathbf{I2\cdot H2O}}$ using transparent van der Waals sphere for interacting atoms. Observed I…O contacts of 2.910(4) Å in $\mathbf{1b}_{\mathbf{I2}}$ and 2.903 (5) Å in $\mathbf{1b}_{\mathbf{I2*H2O}}$ are in good arrangements with similar distances found in CSD (average $I{-}O_{ether}$ = 2.84(8) Å). Symmetry related disorder and all H-atoms have been omitted for clarity.

5. EDX Measurements

Imaging of the samples and analysis of the phase compositions was accomplished using a Zeiss EVO$^{®}$ MA15 Scanning Electron Microscope at the Stellenbosch University. Qualitative analysis and secondary images required gold coating for conductivity and a flat surface. Samples were identified with secondary electron (SE) detector, and compositions were quantified by EDX analysis using an Oxford Instruments$^{®}$ X-Max 20mm2 detector and Oxford INCA software. Beam conditions during the quantitative analyses were 20 KV, with a working distance of 8.5 mm and approximately beam current of – 20nA. The counting time was 10 seconds live-time. Pure Co were used periodically to correct for detector drift.

Analysis of the single crystals by EDX was performed on a mixed phase sample, as inferred by a number of the measured spectrums not containing any detectable quantity of the guests which can be attributed to measurements performed on the non-porous monoclinic phase.

Table S1. EDX data for dry I2 crystals

Spectrum	Weight% C	Weight% O	Weight% S	Weight% I	Weight%Total
Spectrum 1	81.96	8.60	8.94	0.49	100.00
Spectrum 2	80.67	12.69	6.42	0.23	100.00
Spectrum 3	81.95	12.05	5.70	0.30	100.00
Spectrum 4	68.48	4.47	21.21	5.84	100.00
Spectrum 5	74.18	10.33	7.08	8.41	100.00

Table S2. EDX data for dry HCl crystals

Spectrum	Weight% C	Weight% O	Weight% S	Weight% Cl	Weight%Total
Spectrum 1	77.34	7.75	14.90	0.00	100.00
Spectrum 2	73.74	7.50	18.76	0.00	100.00
Spectrum 3	74.68	8.53	16.79	0.00	100.00
Spectrum 4	78.26	9.78	11.83	0.13	100.00
Spectrum 5	78.16	13.97	7.82	0.05	100.00
Spectrum 6	77.07	16.83	5.86	0.24	100.00
Spectrum 7	76.47	11.78	11.09	0.66	100.00
Spectrum 8	76.10	6.61	16.85	0.43	100.00
Spectrum 9	78.52	13.22	8.03	0.23	100.00

6. References

1 M. H. Patel, V. B. Patel and P. S Shrivastav, *Tetrahedron Letters* 2008**, 49**, 3087.

2 H. Katagiri, N. Iki, T. Hattori, C. Kabuto and S. Miyano, *J. Am. Chem. Soc.* 2001**, 123**, 779.

3 *SAINT Data Reduction Software*, Version 6.45, Bruker Analytical X-ray Systems Inc., Madison, WI, USA, 2003.

4 *SADABS,* Version 2.05, Bruker Analytical X-ray Systems Inc., Madison, WI, USA, 2002.

5 G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112.

6 L. J. Barbour, *J. Supramol. Chem*. 2001, **1**, 189.

7 International Tables for Crystallography (Ed.: T. Hahn), Kluwer Academic publishers, Dordrecht, The Netherlands, 1996.

8 Cambridge Structural Database, *v*. 5.35. F. H. Allen, *Acta Cryst. B*, 2002, **58**, 380.

9 T. L. Spek, *Acta Cryst. A*, 1990, **46**, 194.