Supplementary Information

*In silico* design of supramolecules from their precursors: odd-even effects in cage-forming reactions

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Tables S1 to S4.
Figure S1. The observed tetrahedral conformer of CC1, showing the two possible helical enantiomers. The $R$ enantiomer of this conformer is shown in red, the $S$ enantiomer in gray; nitrogens are shown in blue. Hydrogen atoms are omitted for clarity. The bottom row shows a single aryl face of each conformer.

1. Experimental details
The synthesis and characterization for CC1 is described elsewhere.$^1$

1.1. Synthesis of CC-propane. To a cooled (0 °C) solution of propane-1,3-diamine (54.4 mg, 1.58 eq) and DMF (1 drop as internal NMR standard) in DCM (50 mL) was added by syringe pump a solution of benzene-1,3,5-tricarbaldehyde (75.2 mg, 1.0 eq) in DCM (40 mL) over 24 h. The resultant mixture was allowed to warm to room temperature and maintained for 72 h to afford a turbid solution. Completion of the reaction was confirmed by $^1$H NMR. Mass spectrometry (MS) and NMR data were obtained directly by in situ sampling of the reaction mixtures. All attempts at isolating the product resulted in significant amounts of insoluble materials being formed. Yields were therefore calculated by use of an internal standard (DMF), which was added to the solution of the aldehyde in DCM prior to addition of the amine. Integrals associated with the aldehyde (-CH=O, 10.22 ppm), before addition, and the imine (-CH=N, 8.14 and 8.22 ppm for CC-propane and CC-butane respectively), at reaction completion, were normalized against the standard to determine the proportion of cage in solution once the reaction was complete. Insoluble material was assumed not to be product. The in situ NMR showed clean, single product with the expected [2+3] stoichiometry, with integration relative to DMF demonstrating a yield of 24 %. The remainder of the product was an insoluble polymer. $m/z = 439.3$ (M+H$^+$); $^1$H NMR: (400 MHz, CDCl$_3$) δ ppm 2.41 (quin, J = 5.0 Hz, 2 H) 3.89 (t, J = 5.0 Hz, 4 H) 7.79 (s, 3 H) 8.14 (s, 3 H).
Attempts at purifying the material by filtration resulted in the material becoming insoluble on isolation. Concentrating the material and then slowly evaporating the solvent also resulted in insoluble material being formed.

We also attempted to adjust the solvent environment post-synthesis: To a colorless, cooled (0 °C) solution of 1,3,5-triformylbenzene (450 mg) in dichloromethane (100 mL) was added, under nitrogen, a solution of 1,3-propanediamine (309 mg) in dichloromethane (130 mL) over 18 h to afford a colorless solution. The resultant mixture was maintained for 120 h. The reaction mixture was concentrated under reduced pressure (1/2 volume) and diluted with methanol, this procedure being repeated three times to afford a clear, colorless solution in which was suspended an off-white solid. This material was found to be insoluble in chloroform after isolation by filtration.

Finally, we attempted to isolate the material by slow crystallisation. Here, samples (prepared by taking the solutions of DMF-internal-standard experiments) were dissolved in DCM, filtered, and placed in 3 dram vials. These were placed into 10 dram vials, to which was subsequently added MeOH, EtOAc, CHCl₃, IPA, Et₂O, iPr₂O, EtOH, acetone, THF, hexane, MeCN or Toluene: The table below shows the results of these attempts at isolation.

| Solvent  | After 3 days | Solubility in CDCl₃ |
|----------|--------------|---------------------|
| MeOH     | Film         | No                  |
| EtOAc    | Ppt          | No                  |
| CHCl₃    | Clear        | -                   |
| IPA      | Film         | No                  |
| Et₂O     | Ppt          | No                  |
| iPr₂O    | Turbid       | -                   |
| EtOH     | No           | No                  |
| Acetone  | Clear        | -                   |
| THF      | Clear        | -                   |
| Hexane   | Film         | No                  |
| MeCN     | Film         | No                  |
| Toluene  | Clear        | -                   |

Solids, where formed, were separated by filtration. None of these solids were found to dissolve in chloroform.
Figure S2. Mass spectrometry data for [2+3] cage CC-propane.

1.2. Synthesis of CC-butane. To a cooled (0 °C) solution of butane-1,4-diamine (64.9 mg, 1.58 eq) and DMF (1 drop) in DCM (50 mL) was added dropwise a solution of benzene-1,3,5-tricarbaldehyde (76.3 mg, 1.0 eq) in DCM (40 mL) over 12 h. The resultant mixture was allowed to warm to room temperature and maintained for 72 h to afford a turbid solution. Completion of the reaction was confirmed by $^1$H NMR. Again, MS and NMR data were obtained directly from reaction mixtures. The *in situ* NMR showed a clean, single product with the expected [2+3] stoichiometry, with integration relative to DMF demonstrating a yield of 27% (using the imine peak at 8.23 ppm). The remainder of the product was insoluble. As for the CC-propane, all attempts at isolating the material resulted in insoluble material being collected. *m/z* = 961.6 (M+H+); $^1$H NMR: (400 MHz, CDCl$_3$) δ ppm 1.60 (m, 12 H) 3.63 (t, J=6.67 Hz, 12 H) 8.01 (s, 6 H) 8.22 (s, 6 H).
1.3. Synthesis of CC-pentane. To a cooled (0 °C) solution of pentane-1,5-diamine (425 mg, 1.5 eq) in DCM (50 mL) was added dropwise a solution of benzene-1,3,5-tricarbaldehyde (450 mg, 1.0 eq) in DCM (40 mL) over 6 h. The resultant mixture was allowed to warm to room temperature and maintained for 120 h to afford a clear, light-yellow solution. Solvents were removed under reduced pressure to afford a pale yellow solid (875 mg, 100 %). Crystals were then grown by immediately dissolving the cage in dichloromethane, before layering with methanol in a glass vial, and leaving the solutions to slowly diffuse which induced the growth of crystals on the sides of the vial over several days. *m/z* = 523.5 (M+H+, 100%); ¹H NMR: (400 MHz, CDCl₃) δ ppm 0.88 (m, 1 H) 1.77 (tt, J = 8.2, 5.2 Hz, 2 H) 3.61 (t, J = 5.2 Hz, 2 H) 7.86 (s, 1 H) 8.09 (s, 1 H).

On attempting to re-dissolve the material from which the sample was taken for analysis, re-dissolution is not complete in chloroform. Hence, the material is stable in solution, but not upon isolation in the solid state.
Single crystal X-ray data for **CC-pentane** was collected on a Bruker APEX diffractometer with 1.5 kW graphite monochromated Mo radiation ($\lambda = 0.7107 \, \text{Å}$). The detector to crystal distance was 60 mm and the temperature of the crystal was maintained at 173 K throughout the data collection. The crystal diffracted to a maximum theta angle of 25.35°. Total reflections collected, 16746, independent reflections 6779 unique (R(int) = 0.0510)); parameters, 352; R1 = 0.0998; wR2 = 0.2020; density, $= 1.122 \, \text{g cm}^{-3}$. The frames were integrated with the SAINT v7.68a (Bruker, 2009). A multi-scan absorption correction was carried out using the program SADABS V2008-1 (Bruker, 2008). The structures were solved and refined with X-SEED, a graphical interface to SHELX (Sheldrick, 2008). The cage structures refined well but the electron density corresponding to solvent molecules was diffuse and, due to the high symmetry, could not be modelled using disordered solvent molecules. Instead, an approximate number of methanol molecules was determined using PLATON/SQUEEZE and their contribution subtracted to the X-ray diffraction data. This corresponds to either 7 methanol molecules, or 6 methanol molecules plus 2 water molecules. Hydrogen atoms were placed in geometrically idealized positions. In the final cycles of refinement, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined with their distances and thermal parameters constrained.

The crystallographic data for the **CC-pentane** methanol solvate is attached as additional supporting information.
**Figure S5.** Single crystal X-ray structure of the CC-pentane methanol solvate, viewed down the y axis (left) and down the z axis (right). The solvent was removed using PLATON/SQUEEZE and is not shown. The structure contains only isolated voids (shown in orange), as estimated from a solvent accessible surface calculated using a probe radius of 1.82 Å (equivalent to the radius of a nitrogen molecule) in Materials Studio 5.0 (Accelrys Inc.). Carbons are shown in grey, nitrogens in blue, and hydrogens in white.

### 2. Computational details

#### 2.1. Conformer searching method

We used the MacroModel (version 9.9, Schrödinger, LLC, New York, NY, 2011) conformer searching tool to search for all the low-energy conformers for each structure. We first validated that this approach finds known alternative conformers for published organic cage systems, and that it gives reasonable relative energies by examining case studies from other imine cages that we have reported previously (see Section 2.4). The procedure uses a low-mode (LMOD) sampling approach which follows the low frequency eigenvectors of the molecule. This has been used previously to examine cyclic alkanes. We used 50,000 search steps for [2+3] molecules and 500,000 steps for the larger [4+6] molecules. The maximum and minimum move distances were 3 and 12 Å, with all structures within an energy window of 50 kJ mol\(^{-1}\) of the lowest energy structure being retained. This number of steps was chosen because repeats of the calculations found no new low energy structures, with each conformation sampled multiple times within an individual run. For geometry optimization, the convergence criterion was a remaining RMS force of 0.05 kJ mol\(^{-1}\) Å\(^{-1}\). These cages can often exist in two alternative enantiomers (R and S) related by helical chirality; since these have equivalent energies, we only retained one mirror-image conformer. We used an automated procedure (Section 2.5) to check for conformations with an internal ‘pore’, defined here as a spherical space with a radius of >2.5 Å. If none was found, then we repeated the search with an additional 250,000 steps and a search window of 500 kJ mol\(^{-1}\) in order to see whether any structures with an internal void could be found lying higher in energy.

We applied a final refinement of the structures and energies by optimizing the resulting molecular structures with DFT-D3 calculations performed in CP2K\(^{10}\) with the PBE functional,\(^{11}\) TZVP-MOLOPT basis sets,\(^{12}\) GTH-type pseudopotential,\(^{13}\) a plane wave grid cutoff of 400 Ry, a cubic box of length 50 Å, and the Grimme-D3 dispersion correction.\(^{14}\) This procedure was applied to any structure within 25 kJ mol\(^{-1}\) of the lowest energy conformer, which we determined as the maximum error in the
energy difference between structures for the OPLS force field (see Section 2.3). We have previously used this DFT setup to reliably reproduce the structure and energetics of porous imine cages in both the solid state\(^5,^{15}\) and as single molecules and dimer pairs.\(^4,^{16}\)

### 2.2. Performance of OPLS forcefield for porous organic imine cages

Many of the commonly available, transferable forcefields perform poorly at reproducing the structures of porous organic imine cages, either because they do not contain the relevant parameters for, or are poorly parameterized for, the angles and torsions around the imine bond. Hence, optimization of the cage molecules by these forcefields, such as UFF\(^5,^{17}\) and PCFF\(^6,^{18}\), severely distorts the tetrahedral structure of the cages upon minimization. However, upon testing the OPLS all-atom forcefield (Optimized Potentials for Liquid Simulations)\(^7,^{19}\) it performed very well at reproducing both the molecular structures and molecular energies of a range of known imine cages. The OPLS forcefield was developed for organic and biomolecular systems, with the focus on fitting being the energetics of conformers, intermolecular gas phase energies and testing against thermodynamic properties of pure organic liquids, particularly heats of vaporization and densities.

We took single cage molecules from the single crystal X-ray structures of several published imine cages that were also formed using 1,3,5-triformyl benzene: CC2 (1,2-propylenediamine)\(^8,^{20}\), CC3 (1,2-diaminocyclohexane)\(^10,^{20}\), CC4 (1,2-diaminocyclopentane)\(^11,^{21}\) and CC9 (1,2-diphenylethlenediamine)\(^12,^{22}\). All of these cages have a \([4+6]\) ratio of aldehyde to amine precursors. We then geometry optimized these isolated cage molecules using OPLS-2005 using Macromodel, part of the Schrodinger software package (MacroModel, version 9.9, Schrödinger, LLC, New York, NY, 2011), until the remaining force was less than 0.05 kJ Å\(^{-1}\) mol\(^{-1}\). Figure S6 shows overlays of the molecular structure from the X-ray data and the OPLS minimized structures. The structures are very well reproduced, in particular the core cage structures. The root mean square displacements, including hydrogens, are 0.072 Å (CC3), 0.142 Å (CC4) and 0.206 Å (CC9). The CC2 structure cannot be compared in this quantitative fashion due to the disorder in the methyl positions across the two possible vertex positions in the single crystal X-ray diffraction structure. There is some small difference in the cyclopentane vertices of CC4, but these are disordered in the crystal structure in any case. There are also some differences in the phenyl group torsions on the vertices of CC9, where there is presumably facile rotation and a flat potential energy surface. The latter is not considered to be a problem because this type of fragment is not present in the new alkanediamine cage molecules examined here, although this could become an important consideration in building a more generic methodology. Finally, from previous DFT\(^+\)D calculations on the molecular structures, the two lowest energy CC1 conformers (with T and C\(_3\) symmetry, respectively) were found to lie 13 kJ mol\(^{-1}\) apart\(^9,^{13}\). Geometry optimized structures of these two molecules in OPLS were found to lie 15 kJ mol\(^{-1}\) apart, a good agreement with this DFT value. Taken in combination, these results gave us confidence that OPLS could be used for the reliable description of both the 3-D structures and the relative energies of the new organic cages reported in the main text.
Figure S6. Overlays of the molecular cage structures taken from single crystal X-ray structures (blue) and the OPLS-minimized structures (red). Hydrogens are not shown.

2.3. Relative energies of OPLS and DFT
In order to select which band of low-energy structures from the OPLS conformer search to refine using PBE/TZVP-MOLOPT DFT+D3 calculations, it was first necessary to establish a confidence level in the forcefield. By determining the maximum magnitude of the energetic reordering of the structures from OPLS to DFT calculations, it can be ensured that the ‘true’ lowest energy structure is not missed because it lies too far above the lowest energy OPLS structure. To do this, the energies of the [2+3] and [4+6] molecules formed from 1,3,5-triformylbenzene (TFB) and 1,5-diaminopentane were compared from both OPLS and DFT calculations. The results are shown in Figure S6 and Tables S1 and S2. These data show that there is some reordering of the relative energies of the structures, with the absolute numbers being fairly small. For the [2+3] structures, the maximum change in relative energy was found to be 8.2 kJ mol\(^{-1}\), and for the [4+6] structures, the maximum change was 11.4 kJ mol\(^{-1}\). On this basis, the confidence level in the forcefield was determined to be 20 kJ mol\(^{-1}\). Hence, for all systems, all structures from the OPLS conformer search that were within 20 kJ mol\(^{-1}\) of the lowest energy structure were reoptimized in DFT calculations in order to find the final, lowest energy conformer.
Table S1. Reordering of the structures of [2+3] molecules formed from TFB and 1,5-diaminopentane based on OPLS and DFT calculations.

| OPLS ranking | OPLS $E_{\text{rel}}$ (kJ mol$^{-1}$) | DFT ranking | DFT $E_{\text{rel}}$ (kJ mol$^{-1}$) | Difference (OPLS-DFT) |
|--------------|----------------------------------|-------------|-----------------|----------------------|
| 1            | 0                                | 4           | 0               | 0                    |
| 2            | 0.3                              | 1           | -7.9            | -8.2                 |
| ~3           | 2.7                              | 2           | -1.5            | -4.2                 |
| ~3           | 2.7                              | 3           | -1.4            | -4.1                 |
| 5            | 3.7                              | 5           | 10.0            | 6.3                  |

Table S2. Reordering of the structures of [4+6] molecules formed from TFB and 1,5-diaminopentane based on OPLS and DFT calculations.

| OPLS ranking | OPLS $E_{\text{rel}}$ (kJ mol$^{-1}$) | DFT ranking | DFT $E_{\text{rel}}$ (kJ mol$^{-1}$) | Difference (OPLS-DFT) |
|--------------|----------------------------------|-------------|-----------------|----------------------|
| 1            | 0                                | 5           | 0               | 0                    |
| 2            | 2.1                              | 1           | -8.7            | -10.8                |
| 3            | 3.0                              | 4           | -1.8            | -4.8                 |
| 4            | 3.5                              | 2           | -7.9            | -11.4                |
| 5            | 3.9                              | 3           | -2.4            | -6.3                 |

Figure S7. Reordering of the structures of [2+3] (left) and [4+6] (right) molecules formed from TFB and 1,5-diaminopentane from the OPLS energies and the PBE/TZVP-MOLOPT DFT+D3 energies. The energies are relative to the lowest energy conformer. The first points (on the left) are for OPLS, and the second points (to the right) are the DFT results.

2.4. Validation of conformer searching approach for porous organic cages
To validate the conformer searching procedure, several test case studies were identified, based on porous imine cages that have been reported previously. These test cases were:

i) CC1 – there are two alternative T symmetry [4+6] cage molecules (enantiomers labeled $R$ and $S$ have helical chirality); these enantiomers, of course, have the same energy. There is an additional $C_3$ conformer that lies by ~13 kJ mol$^{-1}$ higher in energy.

ii) CC5 – there are two alternative T symmetry [4+6] cage molecules ($R$ and $S$ enantiomers, again isoenergetic); the lowest energy structure is expected to be
shape-persistent with a cavity, as exemplified by the highly porous nature of the bulk material for this cage.\textsuperscript{15}

iii) \textbf{CC7} – this is a large [8+12] cage molecule with a shape (in its solvate form) of a rhombicuboctahedral capsule, and a lower energy “collapsed” structure that lacks a permanent internal cavity, demonstrating that this cage, unlike \textbf{CC1} and \textbf{CC5}, is not shape persistent.\textsuperscript{23}

The conformer searching procedure outlined in the main text was carried out on structural models built from the relevant precursors (that is, not taken from single crystal X-ray diffraction data) in order to replicate our approach for the new molecules synthesized in this study, and to reflect the procedure that would be used for a hypothetical molecule that has not yet been synthesized. For these systems, only 15,000 steps were used in the conformer searching procedure. In brief, the results were as follows:

i) For \textbf{CC1}, both of the tetrahedral enantiomers were found with the same energy (to within a fraction of a kJ mol\textsuperscript{-1}). In addition, another conformer was found with C\textsubscript{3} symmetry, where some of the C\textsubscript{aren}-C\textsubscript{imine}-N\textsubscript{imine} torsions were flipped by 180\degree, which lay 13 kJ mol\textsuperscript{-1} higher in energy than the T conformers as calculated in OPLS. Both conformers were excellent matches with the relevant single crystal X-ray diffraction structures, and no lower-lying ‘collapsed’ structures were found, validating the known shape-persistence for \textbf{CC1}.

ii) For \textbf{CC5}, the tetrahedral enantiomers were again found as the lowest energy structures, with the next conformer lying 15 kJ mol\textsuperscript{-1} higher in energy; this had a similar structure, with small rotations of the phenyl groups of the triphenylamine cage face. Again, this molecule was correctly determined to be shape-persistent and no low energy “collapsed” structures were found.

iii) For \textbf{CC7}, the lowest energy conformer was found to be a collapsed structure with no internal cavity. More than 100 kJ mol\textsuperscript{-1} higher in energy (by OPLS) was found the rhombicuboctahedral capsule structure, which was observed in single X-ray crystal diffraction data for the solvated molecule. This is in agreement with the observed lack of shape-persistence for this larger cage, which collapses upon desolvation.

In summary, this conformational searching approach with OPLS successfully reproduces the desired structures, relative energies, and experimental shape-persistence (or lack of) for all three case studies.

\textbf{2.5 Identifying conformations that contain an internal void: screening for shape-persistence}  

In order to automatically determine whether the various conformations found during the conformer searches for [4+6] molecules contained an internal void, we wrote a PERL script to determine the largest sphere that could fit within the center of the cage. First, the center of mass of each molecule was calculated, and then the shortest distance between this center of mass and any atom of the molecule was determined. This distance, minus the van der Waals radius of the atom (C = 1.7 Å, H = 1.2 Å, and N = 1.55 Å), was then defined as being the radius of the largest sphere that can fit
within the cage molecule. A molecule was then deemed to have an internal void if this radius was greater than 2.5 Å. This is equivalent to the cage molecule being able to encapsulate small guests such as H₂, N₂, CO₂, Xe, and common organic solvents.

The measured void radius for CC1 here is 2.76 Å (Table S4), and this cage is known to encapsulate solvents such as dichloromethane and ethylacetate²⁴. Hence, since all the “inflated” conformations for the other cage molecules studied here have a void larger than this, it seems reasonable to assume that the solvents used here (methanol, DCM, ethyl acetate, ethanol and chloroform) are able to act as scaffolds for any of these structures.

Figure S8. The largest sphere (in orange) that can fit within the internal void of the CC1 molecule. CC1 is shown with a space filling representation, omitting hydrogens, with transparency to show the void sphere.
3. Computational results

3.1. Structures and energies of low energy conformers for alkane cages

Table S3. Relative energies of the low energy conformers, expressed per [2+3] unit, from DFT+D3 calculations for [2+3] and [4+6] precursor combinations. The lowest energy conformer for each case is highlighted in **bold**. The right hand column gives the relative energy for the lowest energy conformer found with no internal cavity, if any.

| Alkane diamine | [2+3]  | [4+6]  |Collapsed [4+6] |
|---------------|--------|--------|----------------|
| 1,2 ethane    | 0      | -61, -46 | n/a            |
| 1,3 propane   | 0      | +21     | -6             |
| 1,4 butane    | 0, +2  | -37, -35, -30 | -56         |
| 1,5 pentane   | 0, +6, +8 | +48, +54 | -20            |

3.2. Void sizes

Table S4. Radius of the spherical internal void (Å) of the lowest energy conformation for each precursor combination. All [4+6] combinations can accommodate solvent, whereas, with the possible exception of the 1,5-pentane system, the [2+3] cages are unlikely to be able to accommodate solvent guests.

| Alkane diamine | [2+3]  | [4+6]  |Collapsed [4+6] |
|---------------|--------|--------|----------------|
| 1,2 ethane    | 0.00   | 2.76   | n/a            |
| 1,3 propane   | 0.65   | 4.39   | 0.00           |
| 1,4 butane    | 0.52   | 3.97   | 0.00           |
| 1,5 pentane   | 1.32   | 5.42   | 0.06           |

3.2. Predicted structures

We include the Cartesian coordinates for the predicted **CC-propane** and **CC-butane** molecular structures, for reference with any future, solved structures from experiment. The relevant cif files can also be supplied upon request.

**CC-propane:**

N   23.1302014743   22.0767429329   21.9932156620
C   23.3336112351   21.032672891    21.0037001030
C   24.5538408211   21.3144546998   20.1102832217
C   25.9235629668   21.0930428497   20.7742209143
N   26.2468721219   22.1467296645   21.7200251792
H   22.4410557567   21.0166326207   20.3550899999
H   23.4275188679   20.0261328224   21.4642518973
H   24.4967376848   22.3481324962   19.7376573755
H   24.4911435006   20.6479197167   19.2354107435
H   26.6886463641   21.1167478597   19.9796803269
CC-butane (structure with an internal void):

N  24.3558624743  27.9307686318  31.8769682091
C  23.736415562  27.2332431232  32.9907834961
C  24.2486432357  25.794593119  33.0972817896
C  23.8426377445  24.9158040923  31.9101293447
C  24.3352705203  23.4719279381  32.0581011877
N  23.8690670629  22.6457302656  30.9581323567
C  22.6280365912  27.2382959496  32.9240495827
C  24.0153512826  27.7731376076  33.9146257611
C  23.8601368632  25.354305152  34.0326547308
C  25.3465931100  25.814536843  33.188516958
H  22.7457713313  24.9053423694  31.801880366
Figure S9. Calculated structures of the lowest energy conformer for both the [2+3] and [4+6] cages formed from reaction of each alkanediamine with 1,3,5-triformyl benzene. If a collapsed [4+6] structure was found, this is also shown.
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