Towards Stable Porous Crystalline Phases of Molecular Belts

Marco Bernabei,[a*] Raul Perez Soto,[a] Ismael Gomaez Garcia,[a,b] Maciej Haranczyk[a]

[a] IMDEA Materials Institute, C/Eric Kandel 2, 28906 - Getafe, Madrid, Spain

[b] Departamento de Materiales, Universidad Carlos III de Madrid, Avda. Universidad 30, 28911 Leganés, Spain

Supporting Information

Content

S1.MD simulations to assess the thermal stability of desolvated crystal structures.

In order to investigate the thermal stability of the experimental crystal structures of M1 (CSD Refcodes: YELKUW, YELLAD, EHETIV) we first manually removed the solvent molecules from the the corresponding CIF file downloaded from Cambridge Structure Database (CSD) to create a fully desolvated structure. In figure S1 we depict a projection along the b-axis of the filled unit cell of YELKUW including solvent (left panel) and without solvent (right panel).

The desolvated structures were then used to build a supercell (see Fig. S2 top-left panel as an example for the desolvated YELKUW structure) containing 180 molecules and that constituted the starting point of the molecular dynamic (MD) simulations with periodic boundary conditions carried out with the GROMACS package. A time step of 1.5 fs was used and the Berendsen thermostat and barostat were employed to keep the system at P=1atm and T=300K. The OPLS_2005 force field was employed to model both inter and intramolecular interactions. At the end of a 1ns length simulation we visually inspected the last snapshot and we observed that the system lost the initial symmetry and evolved to a denser phase, with an increase of about 15 % in density and a decrease of about 50% in the value of the PLD.

The same simulation protocol involving the construction of a supercell (Fig. S2 bottom panel) and the subsequent MD simulation was also applied to assess the thermal stability of the crystal phases αM1, αM2, βM1 and βM2 (Figure 3 in the main text) predicted by our CSP approach described in the main text and section S3.

As an example, in the bottom panel of figure S2 we depict a 4x5x4 supercell (180 molecules) of the predicted βM1 structure (see section S5 for the corresponding crystallographic information) at the beginning (left) an at the end (right) of a 1ns MD simulation at P=1atm and T=300K. Simulations details are described above. In this case, at the end of the simulation run we observe that the system still conserves the initial symmetry, the density decreases of a 2.5 % due to thermal effects and that the value of the PLD barely changes.

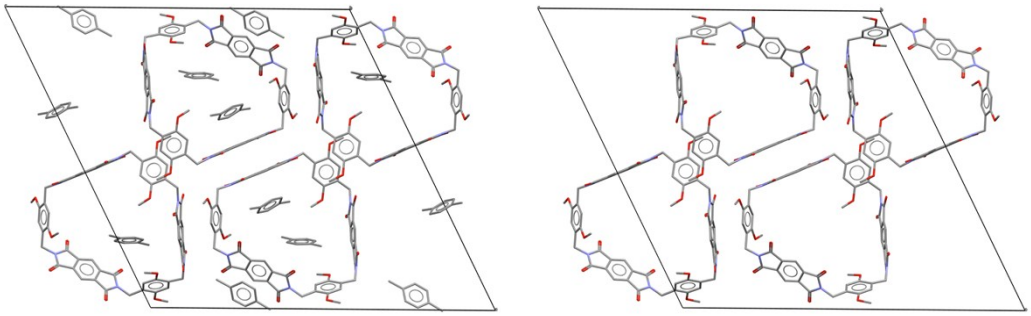

Figure S1. Projection along the b-axis of the filled unit cell of the experimental structure YELKUW including solvent (left panel) and without solvent (right panel). Hydrogen atoms are not included for clarity.

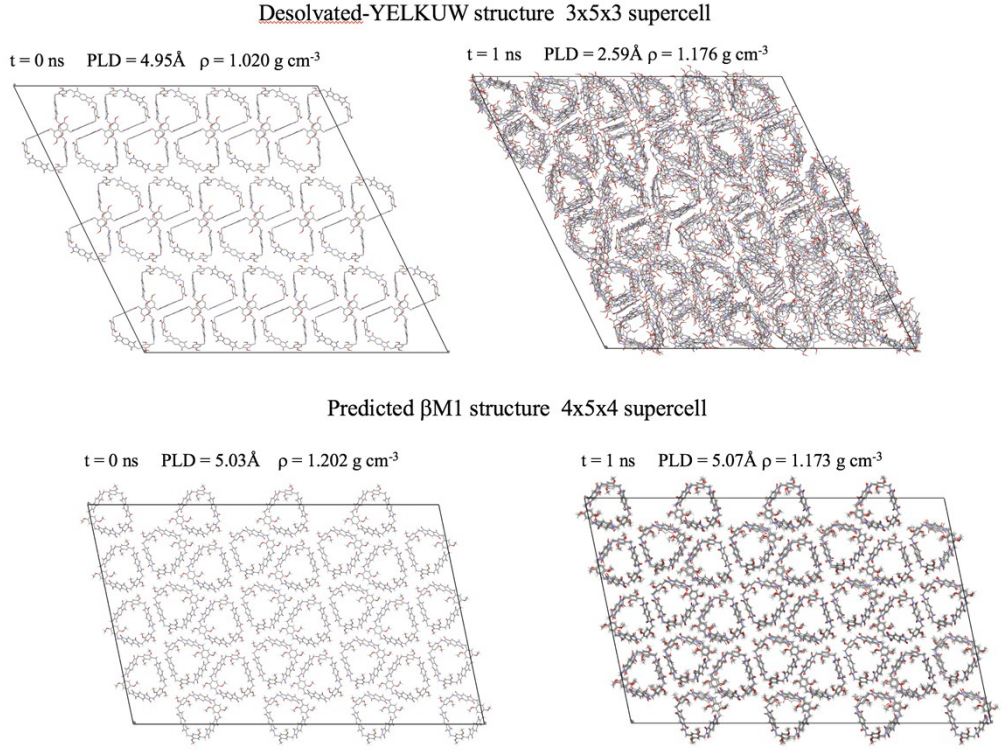

Figure S2. **Top panel**: Projection along the b-axis of a 3x5x3 supercell of the manually desolvated experimental YELKUW structure at the beginning (left) an at the end (right) of a 1ns MD simulation**.** **Bottom panel**: Projection along the b-axis of a 4x5x4 supercell of the predicted ßM1 structure at the beginning (left) an at the end (right) of a 1ns MD simulation.

S2. Single molecule conformational analysis

The coordinates of molecule M1 and M2 where first generated with the Schrodinger's tool LigPrep (1), which is a robust collection of tools designed to prepare high quality, all-atom 3D structures for molecules of up to 900 atoms, starting with SMILES sequences, 2D or 3D structures in SD (.sdf) or Maestro (.mae) format.

The molecules generated with LigPrep where submitted to a conformational search routine that performs an initial cycle of several short MD simulated annealing runs followed by a conformational sampling by means of the LargeLow-Mode sampling technique implemented in the Schrodinguer's MacroModel suite (1).

The conformational search uses the OPLS_2005 force field (FF) to model intramolecular degrees of freedom and non-bonded interactions. The OPLS_2005 FF is an enhanced version of the original OPLS force field, and is developed by the Schrodinger company to provide a bigger coverage of organic functionality. In particular, intramolecular parameters have been fit to reproduce the conformational energies derived at a higher level of quantum theory for a large set of organic molecules.

To assess the quality of the intramolecular modeling provided by the OPLS_2005 force field the generated conformers of M1 and M2 within an energy range of 30kJ/mol from the lowest energy one where subsequently optimized with DFT-B3LYP/6-31G* calculations performed with the Schrodinger's Jaguar *ab-intio* package (1).

In figure S3 we depict the comparison of the OPLS_2005 conformers (red lines) to the DFT-optimized ones (blue lines) and we quantify the structural differences by measuring the Root-Mean-Square-Deviation (RMSD) of atomic positions for heavy atoms. The agreement is good for both M1 and M2 low energy and high energy conformers.

Finally, we note that the diameter of the cavity of both lowest energy conformers (ΔE = 0.0 kJ/mol) of M1 and M2, measured with our pore detection algorithm described in Ref. 2, takes the value of 8.62Å and 8.74Å. The intrinsic molecular pores of the high energy conformers (ΔE = 22.3 kJ/mol for M1 and ΔE = 19.4 kJ/mol for M2) are smaller though, their diameters take the values of 6.2Å and 6.3Å for M1 and M2, respectively.

The molecular geometry of the lowest energy conformer where adopted to start the initial random search at the beginning of the Crystal Structure Prediction procedure. See section S3 for further details.

Further technical details about LigPrep, MacroModel conformational tool and our pore detection algorithm can be found in the ESI of Ref. 2.

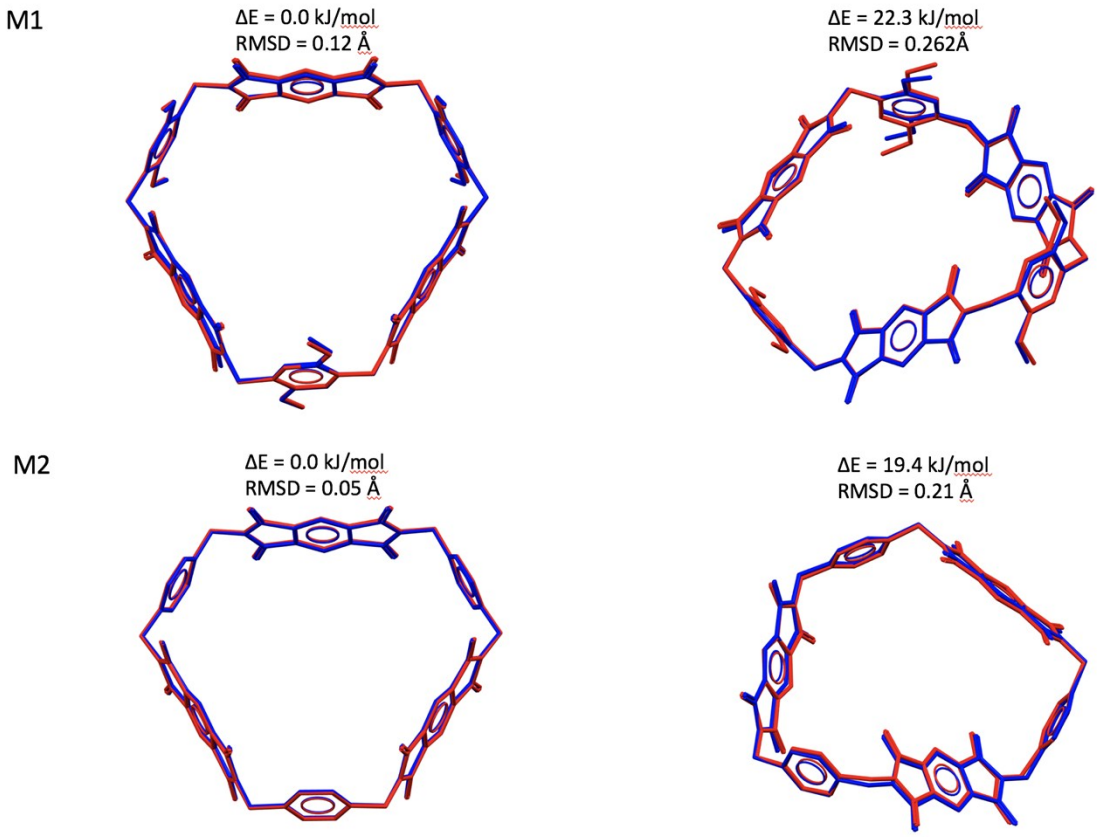

Figure S3. Overlay of the molecular geometries of the OPLS_2005 conformers (blue) and the corresponding DFT-B3LYP/6-31G* optimised ones. The values of the Root-Mean-Square deviation of atomic position show good agreemet.

S3. Crystal structure prediction

Crystal structure prediction (CSP) calculations presented in this work were performed using a random search technique implemented in the UPACK (Utrecht Crystal Package) program suite (3). UPACK provides hypothetical crystal structures by approximating the free energy of the crystal with a static lattice energy and minimizing it by using a molecular force field (FF). The latter is defined as the sum of an intermolecular potential, consisting of van der Waals and Coulomb terms, and a combination of intramolecular energy terms, which account for molecular flexibility

We employed the widely used transferable OPLS_2005 force field to model the lattice energy for the systems considered in this study. In the OPLS_2005-FF framework, the intermolecular potential energy is modeled as the sum of Lennard-Jones and Coulomb terms while intramolecular interaction includes stretching, bending and torsional terms

As stated above, static lattice energy minimization is at the core of the UPACK method for crystal structure prediction simulations. Energy minimization steps are normally performed by a combination of the steepest descendent method followed by a

certain number of conjugated gradient minimization steps. Intermolecular interactions are truncated at a certain cut-off based on the charged groups distance and the Ewald summation method is employed for Coulomb and Lennard-Jones r^{-6} dispersion terms.

A full CSP study with UPACK was carried out in three steps:

Step 1. In the first step, we generated candidate structures (5000 are usually sufficient) by means of a random search method combined with a rough energy minimization (using a cut-of 8Å for intermolecular interactions). Initial structures are generated for a set of selected space groups with Z'=1 molecules in the asymmetric unit.

The number of degrees of freedom for the random search comprehends up to 6 variables for the unit cell plus 6 degrees of freedom that describe global translation and rotation of the molecule in the unit cell. For molecules with rotatable bonds further degrees of freedom are considered during the random search to account for different molecular conformations.

The total number of degrees of freedom, D, cannot be arbitrarily large for the random search method to be successful. Indeed, it was empirically noticed[9] that the random search method started to fail when the total number of random variables is around 20.

Step 2. During this step, a minimization of the static lattice energy with a larger cut-off of 20.0Å w.r.t all the degrees of freedom was used to further refine the structures generated in Step 1.

Step 3. Equivalent structures resulting from different initial orientations of Step 1 were grouped together by the means of a clustering algorithm based on interatomic radial distribution functions as implemented in UPACK. The final set of unique structures was finally ranked according to their lattice energy relative to the lowest minimum found.

Our aforementioned procedure was tested and validated by performing the CSP calculations for the well-known porous imine cage CC1. CC1 cage molecule is one of a series of porous organic shape-persistent cages with large internal cavities synthesized in the group of Prof. Cooper of University of Liverpool, UK. These molecules have been of great interest especially for their capacity to tune porosity when exposed to different solvents (4). In our CSP validation study the two experimentally observed desolvated polymorphs CC1-α' (non-porous) and CC1-β'(H_2 selectively porous) were predicted in the leading-edge of the low energy region of the energy landscape. More details about our validation procedure can be found in the ESI of Ref. 2

Motivated by the results for porous cage CC1, we decided to apply UPACK prediction procedure to study the porosity properties of the predicted structures for the molecules M1 and M2 introduced in the main text.

S4.H-bond patterns in the βM2 predicted structure.

In the case of the βM2 crystal phase, the lack of methoxy groups in M2 (w.r.t M1) enables the formation of intra (blue dashed line in Fig. S4) and inter-molecular (red dashed line in Fig. S3) hydrogen bonds (HB) by pairing the acceptors oxygen atoms with the phenyl H donor atom. According to the following geometric definition an HB is formed if the distance H··O is less then 2.6 Å and the angle CH··O is larger than 90˚ (5,6)

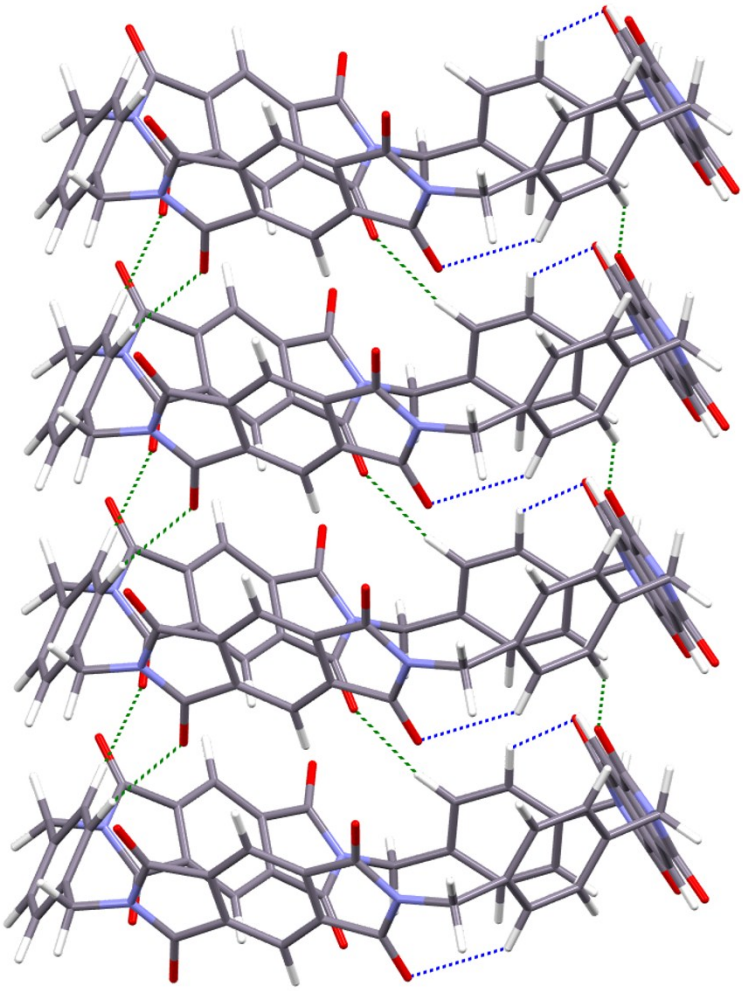

Figure S4. Side view of the 1D tubular channel in structure βM2. Intra and inter-molecular H-bond patterns are displayed as dashed green and blue line, respectively. Grey, blue, red and white represent carbons, nitrogen, oxygen and hydrogen atoms, respectively

S5. **Crystallographic information for the predicted structures αM1, βM1, αM2, βM2.**

Below we report the crystallographic information for the predicted structures αM1, βM1, αM2, βM2 in the CIF data format and depicted in Figure 3 in the manuscript.

- **Crystallographic information for the predicted structure αM1**

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alpha-M1
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   -x,-y,-z
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C     0.331285  0.335403  0.697657
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- **Crystallographic information for the predicted structure αM2**

alpha-M2
CIF file relative to the alpha-M2 predicted structure
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H 1.452672 0.836635 0.266920
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- **Crystallographic information for the predicted structure βM1**

beta-M1
CIF file relative to the beta-M1 predicted structure
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- **Crystallographic information for the predicted structure βM2**

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H 0.330354 0.553803 0.749243

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