

# Three-Dimensional Uracil Network with Sodium as a Linker

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## Supporting Information: Computational modeling

Density Functional Theory calculations carried on in this work were done using the level, in all cases the Tkatchenko-Scheffler van der Waals correction (vdW) method for accuracy. The simulation box in all cases included (unless something different is stated) a grid spacing of 0.18 Å and a vacuum distance from the last atom of 8.0 Å. The optimizations were done using a BFGS algorithm until the forces were lower than 0.01 eV/Å. For the small structures a Minima Hopping method was used, taking the first five structures. In the rest, a single minimization method was used for the structures.

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The first level of calculation corresponds to the analysis of a simple uracil-cationic sodium system ( $\text{U-Na}^+$ ). We have found two stable structures (see Fig. S1), in both cases, the sodium binds the oxygen atoms. The most stable system binds the sodium to the O4 and the second to the O2. The minima structures were found using the Minima Hopping algorithm.

The binding energy for the two systems is 1.62 eV (37.36 kcal/mol) and 1.43 eV (33.07 kcal/mol) respectively. Following the idea that after the interaction with the sodium cation, the whole structure should be fully neutral, we have calculated the deprotonated uracil U and the sodium ion. The deprotonation favors the double bonding of the ion with both nitrogen and oxygen (see Fig. S2). The final product upon deprotonation is more energetically stable than the respective fully cationic structure. It is worth to mention that this reaction implies a production of hydrogen molecules as a remaining product during the formation of the periodic structure. In the Fig. S3, a complete reaction path for uracil and the cationic sodium is depicted. From uracil (U) and sodium ( $\text{Na}^+$ ) into the compound  $\text{U}+\text{Na}^+$  and then to the deprotonated uracil ( $\text{U}^*$ ) with sodium cation  $\text{U}^* + \text{Na}^+$ .

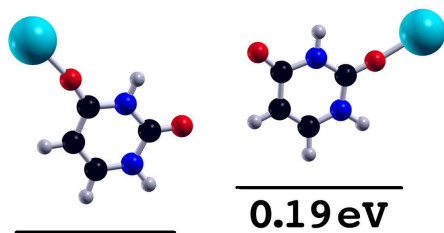


Figure S1: Two stable Uracil- $\text{Na}^+$  structures. The binding energies are 1.62 eV (37.36 kcal/mol) and 1.43 eV (33.07 kcal/mol) respectively.

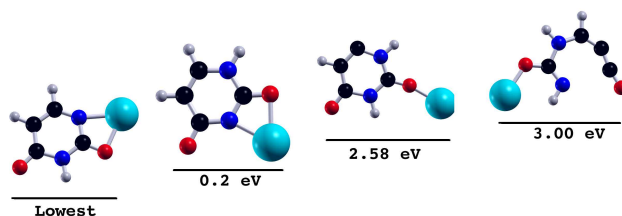


Figure S2: Deprotonated uracil-sodium structures in order of stability.

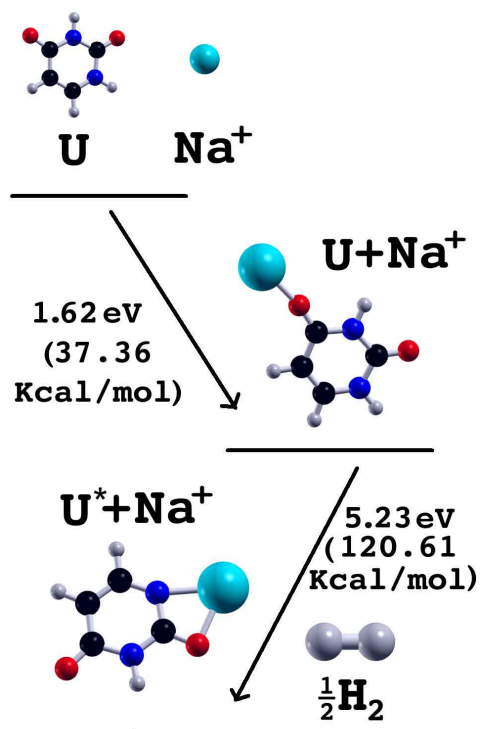


Figure S3: Reaction path of uracil and sodium cation.

# Supramolecular uracil complexes: tetrameric configuration

One of the first attempts to describe the aggregation of uracil compounds follows the idea that the nucleobases must form a stable structure previous to the addition of the molecule that releases the sodium cation. Therefore, if there is some periodic structure that incorporates the cation, the possible site should include a bond with the oxygen presents in the uracil, in particular the O2 site. We have explored a similar configuration to the reported by Fallon *et al.* in 1973, found in 5-fluorouracil.

Indeed, this structure can be extended to trap molecules, however in our version, the presence of hydrogens in the central area (H5 and H6) make the zone electrostatically repulsive for the sodium cations (see Fig. S7).

We have combined four uracil molecules in four different (U4). We have mixed up the two possible ways of bonding to form a tetrameric symmetry in four representative structures as follows: 1. Bonded fully through O2-H1', 2. fully through O4-H5', 3. through two O2-H1' and two O4-H5' and 4. through three O2-H1' and one O4-H5'. The most stable configuration is that one where the four uracils are bonded exclusively through O2-H1' bonds (see Fig. S4).

In a similar way, we have explored the possibility of reaction of the sodium cation with the uracil tetramer. In this case, the stability follows the same order of energy than the free cationic tetrameric cases. One of the advantages of the most stable tetrameric structure is that in all configurations the O2 atom is free for interacting with the cation after a slight rotation. Simultaneously the stabilization is enhanced with hydrogen bonds between O2-H1'centers. The final geometry is almost planar. In the Fig. S5, the reaction path for the minimum geometry is presented. The final configuration where one of the N3 loses its hydrogen (see the text in the main document) remains almost planar but the distance from the central sodium towards the oxygen in the deprotonated uracil is lower than the



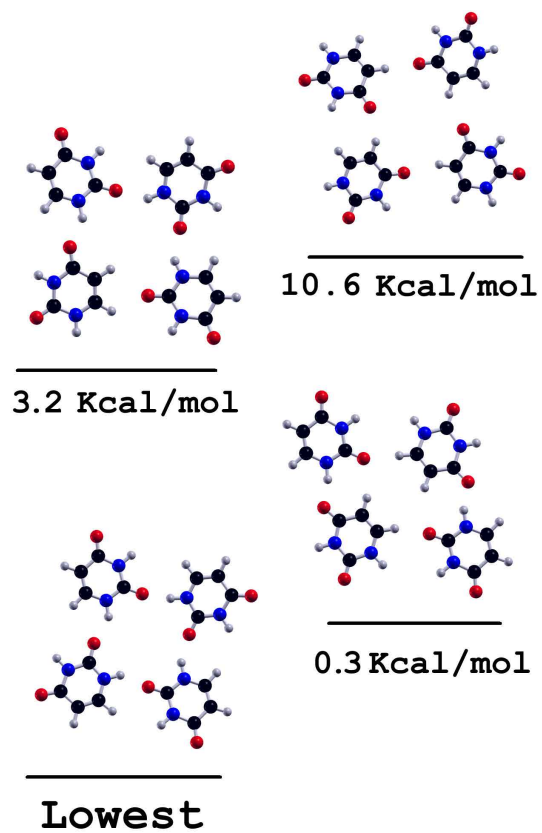


Figure S4: Four studied uracil tetramer structures.

other three uracils. This configuration is the chosen as the most possible description of the experiment data.

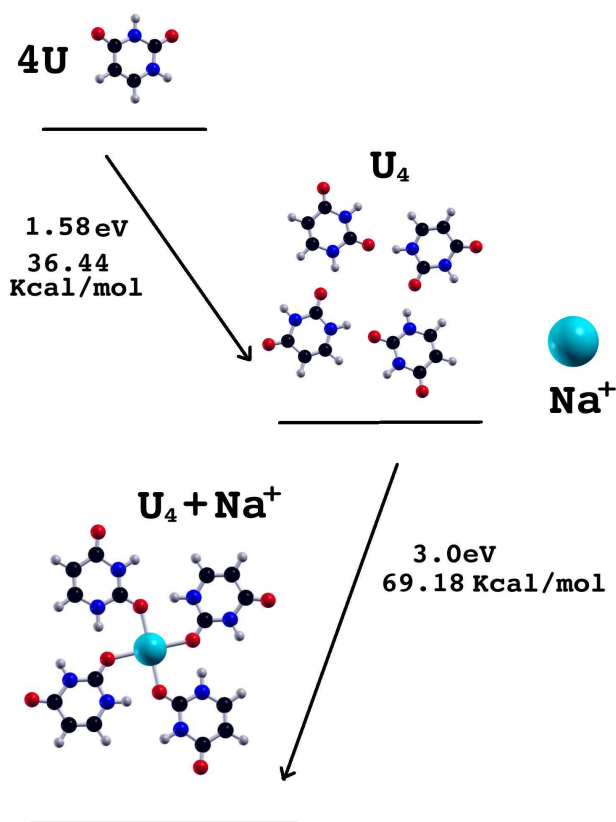


Figure S5: Reaction from single uracil to free uracil tetramer towards the cationic sodium uracil tetramer.

Analysis of the redistribution of charge for the single uracil, the free tetrameric and the sodium cationic tetramer is showed in the Fig. S6. In this figure, the Bader volume is plotted. Interestingly, in all three cases the distribution seems to be equivalent, which means that there is not a big redistribution of the charge during the formation of the free tetrameric structure or during the nitrogen deprotonation and the aggregation of the sodium cation.

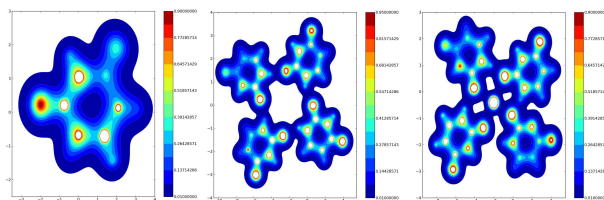


Figure S6: Bader volumes for different configurations. Left: uracil, center: uracil tetramer and right: cationic sodium deprotonated uracil tetramer.

## Aggregation of tetrameric configurations

The challenge of the search of one model for the crystallization of uracil complexes with sodium cations is related with the fact that the global charge of the crystal must be neutral. In the Fig. S7 is presented the supramolecular structure formed by the aggregation of four free tetrameric uracil molecules. The obtained geometry is similar to the reported by Fallon *at al.* It is clear that the stability of this kind of structures in the plane is proportional to the number of formed hydrogen bonds.

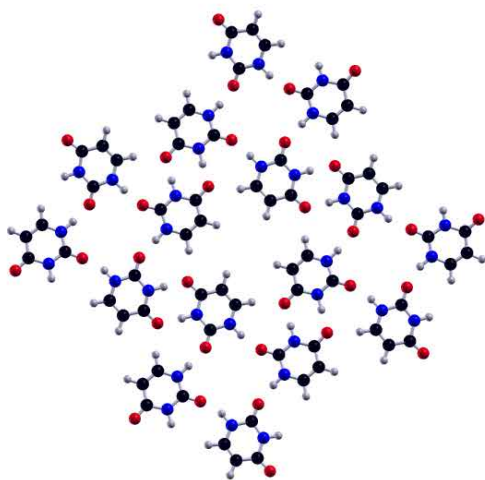


Figure S7: Supramolecular structure composed by the aggregation of four free-tetrameric uracil systems.

We have added four sodium cations in the central region of each uracil tetramer. The stability of the structure is enhanced by the electrostatic interaction between each O2 and the cation. To study the stability of the equivalent neutral structure, we have removed one hydrogen atom (deprotonation) from one uracil at each of the tetrameric structure. We have optimized different cases, by choosing the different position for the removed hydrogen.

The first model is shown in the Fig. S8, here we have removed the H5 in the uracil at the center of the structure (see the enclosed atoms at the figure). This structure is not fully stable because there is a hydrogen transfer from the N1 towards the non-bonded oxygens (O4).

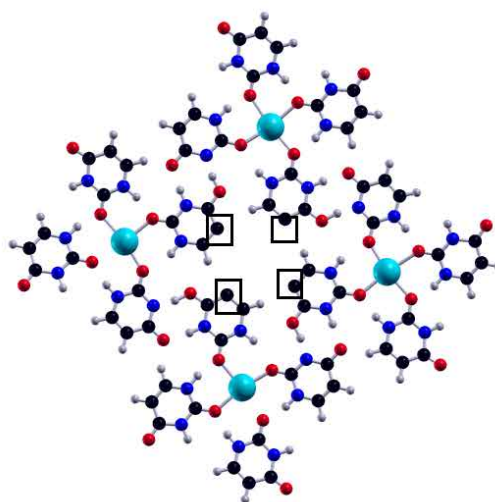


Figure S8: Deprotonated supramolecular structure composed by the aggregation of four  $\text{Na}^+$ -tetrameric uracil systems.

Using the experimental information, we have deprotonated four similar structures by removing one H3 at each tetrameric structure at different symmetries. In the Fig. S9 the studied configurations are showed. In all showed cases the planarity is almost conserved. The lowest structure is the symmetry where the hydrogen is removed from the external circle of uracils (see A in Fig. S9 ). The next stable structure is the symmetry that conserves the periodicity of the tetrameric unit. The other configurations are less stable by removing the hydrogens in the internal circles. The reason because the A configuration is more stable is because this geometry gives the largest separation between the deprotonated nitrogens and the sodium cations. However, the symmetry of the most stable extended system can change because this configuration does not minimize the interaction between charges in the infinite plane. In this case, the most stable configuration is the structure that follows the

periodicity of the tetramer as unit cell (see B in Fig. S9). Analysis of the Bader volume in the aggregated tetrameric structure Fig. S9-B is plotted in the Fig. S10. The redistribution of the charge is very different to the simple tetramer. Zones with more bader charge density are separated with zones mediated with low charge density.

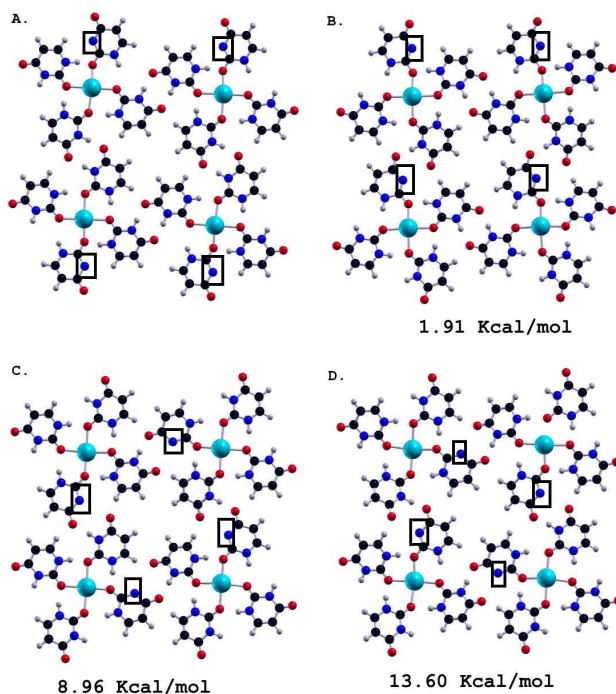


Figure S9: Protonated supramolecular structures composed by the aggregation of four  $\text{Na}^+$ -tetrameric uracil structures. The protonation was done by removing the H3 in one of the uracil in each tetramer. Four in total to neutralize the cationic charges.

## Periodic Calculations

The next step in the research of uracil- $\text{Na}^+$  aggregated films is to find the lattice vectors (x, y, z) for the unit cell that conforms the periodic structure. In this case we use a finer grid of 0.16 Å. First, we have explored with different length vectors in a cubic/orthorhombic cell with parameters a,b, in the xy plane and c in the z direction for the tetramer structure of the Fig. S5. In the z-direction we use 8 Å of vacuum  $z=(0, 0, 8)$ , and we have scanned the x- and y-direction from 12 to 14 Å. Ground state calculations for each step show that the

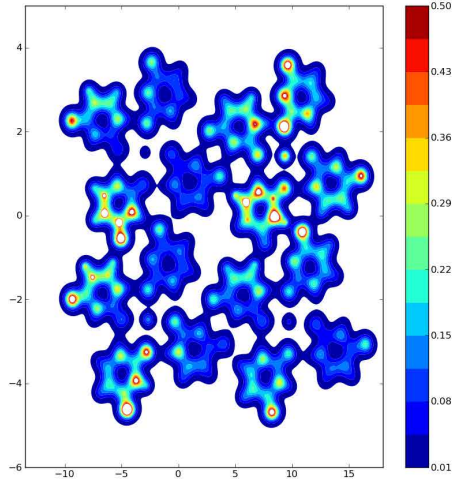


Figure S10: Bader volume for the geometry B of the Fig. S9.

optimized cell has a tetragonal symmetry with  $a = b = 13.1 \text{ \AA}$  (See Fig. S11). A comparison between the obtained extended structure (top-left in Fig. S11) and the relaxed equivalent four tetrameric (structure B in Fig. S9) shows that structures are similar in symmetry but in the non-relaxed 4-tetrameric structure the length of the hydrogen bonds is larger. The stability of the extended structure in the plane should be minor in comparison, however the 4-tetrameric relaxed (Fig. S9-B) can not be extended in a periodic structure without a periodic relaxation because is not stable. In the case of a full geometrical optimization at each iteration, the parameters of the cell changed to  $a = 12.25 \text{ \AA}$ ,  $b = 12.10 \text{ \AA}$  and the tetrameric structure loses its planar symmetry. Once we have the  $x$ ,  $y$  vectors, we search for the  $z$ -vector by scanning in a range up to  $12 \text{ \AA}$  in three cases: scanning the  $x$ -component ( $x, 0, 8$ ), the  $y$ -component ( $0, y, 8$ ) and simultaneously the  $x$ - and  $y$ - components ( $x, x, 8$ ). In all cases, the  $z$ -component was kept to  $8 \text{ \AA}$ . After a comparison of the energy for all configurations the lowest structure is represented by the vectors  $x=(13.1, 0, 0)$ ,  $y=(0, 13.1, 0)$  and  $z=(3.8, 3.8, 3.3)$ . In the Fig. S11 the cell parameters are presented in terms of angles and magnitude of the vectors.

With the vdW correction the energy to split the layers is around 52 kcal/mol per layer. The distance in the top Fig. S11, the final crystalline structure is presented (top and side views) and in the bottom the parameters of the unit cell. In the final structure, the inter-layer distance is around 3.3 Å, therefore a  $\pi$ - $\pi$  interaction is expected between the uracil at different planes. The second source of stability is the interplanar coordination of the sodium cation with the carbon C5 of the uracil in the immediate plane with a distance of 3.2 Å. The final coordination number of each sodium cation is 5.

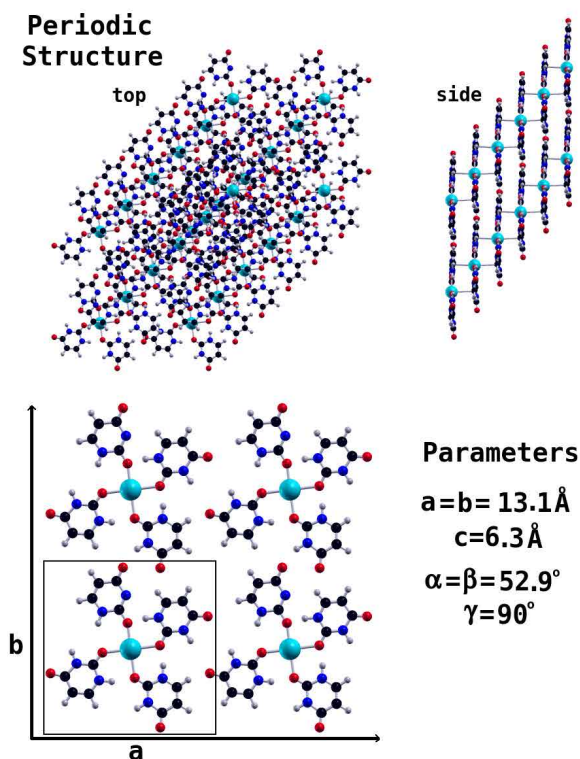


Figure S11: Top: Final periodic structure form by tetrameric uracil-sodium structures (top and side views). Bottom: Extended planar tetrameric structure and parameters of the unit cell.

## Supporting Information: XPS

Table S1: Atomic concentrations derived from the XPS analysis for uracil and Na-uracil. The associated error bars are of the order of  $\pm 10\%$  of the concentration value given.

Element	Uracil	Na-uracil
C (%)	54,7	34,5
O (%)	20,9	28,3
N (%)	24,4	13,9
Na(%)	-	23,3

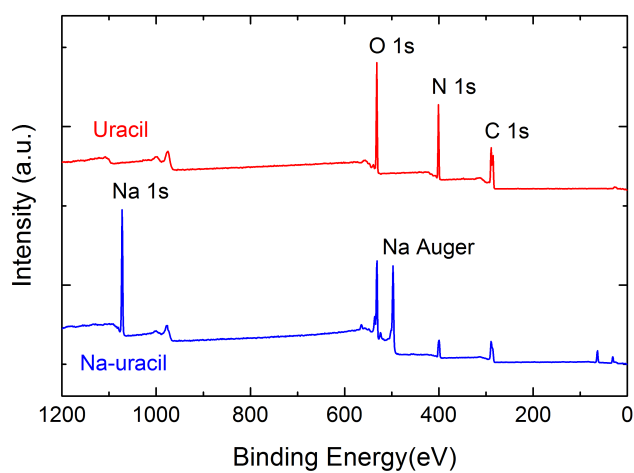


Figure S12: XPS survey spectra for pure uracil and Na-uracil.