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Three-Dimensional Uracil Network with Sodium as a Linker

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Abstract

Here we show that uracil and sodium form a three-dimensional metal-mediated nucleic acid network; it is grown in atomic/molecular layer-by-layer manner using the atomic/molecular layer deposition (ALD/MLD) thin-film technique. The long-range ordered Na-uracil crystalline structure is evidenced as sharp Bragg reflections. Based on density functional theory (DFT) calculations, a tetrameric-like crystal structure is proposed. Na-uracil thin films are fluorescent with a lifetime three orders of magnitude higher than commonly seen for nucleic acid molecules. Our method provides a new approach to designing 3D nucleic acid-metal nanostructures.

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Introduction

Non-covalent molecular interactions have inspired studies of supramolecular organization of *e.g.* nucleic acids on surfaces generating two-dimensional (2D) structures, such as clusters, rows, nanoporous arrays, hierarchical arrangements and multicomponent assemblies.¹⁻³ Carefully selected molecules form artificial nucleic acid structures⁴ through hydrogen bonding, metal-organic co-ordination and van der Waals interactions.⁵⁻¹⁰ Although much progress has been made in creating 2D structures, few studies have succeeded in forming three-dimensional (3D) spatially-controlled molecular arrangements on surfaces. Therefore, a number of approaches have been proposed for generating such 3D molecular arrangements.¹¹⁻¹⁴ While these approaches were able to demonstrate 3D spatially-controlled molecular arrangements in various nanoapplications, none of them considered the influence of hydrogen bonding on 3D nucleic acid-metal molecular deposition.

Hydrogen bonding has been used to produce thin films from heterocyclic compounds.^{15,16} This new class of materials possess excellent optical and anisotropic transport properties. For example, band-like charge transport was observed due to $\pi - \pi$ orbital overlap along the stacking direction of the nucleic acids.¹⁵ Further, heterocyclic compounds have also been found to exhibit fluorescent properties.¹⁷

More recently, much work has been devoted to studying the interactions between metal ions and isolated nucleic acids due to their importance in processes related to DNA replication and transcription.¹⁸ Such metal-mediated base-pair interactions play a major role in the transfer of genetic information, since they allow the base sequence of nucleic acids to encode structural and functional information into materials.¹⁹ The addition of metal ions causes a switch in the nucleic acids. The mechanism underlying this switch is used for designing biosensors and metal-ion-stimulated DNA switches.¹⁹ For example, in the particular case of noble metals, the assembly of metal-mediated DNA strands in single or double strands is highly base-specific,^{20,21} with the final structures resulting from an interplay between the metal-base-solvent interactions. These interactions include not only covalent but also

dispersion interactions that can be accurately simulated within the van der Waals corrected density functional theory.²²

Uracil is one of the four nucleic acids of RNA.²³ It is a solid organic compound of the pyrimidine family (Fig. 1) and forms planar hydrogen-bonded structures (chiral arrays) on surfaces in two dimensions.^{4,24,25} For example, uracil on MoS₂ showed herring-bone patterns originating from hydrogen-bonded dimer formation.²⁴ Such structures closely resemble three-dimensional uracil crystal. When uracil acts as a ligand, the stability of the compound is influenced by the energetics of the different binding sites, *i.e.* the metal-O and metal-N bond strengths, as well as the different hydrogen bonding sites.²⁶

Figure 1: Uracil molecule and the labeling of its constituent atoms, carbon (black), nitrogen (blue), oxygen (red) and hydrogen (grey).

In particular, alkali metal ions are known to interact with phosphate groups of the nucleic acid chain and such an interaction results in a stabilizing effect; Rodgers *et al.*^{27,28} have reported an exhaustive study of Na⁺ ion interactions with uracil. However, to the best of our knowledge none of these studies have attempted to combine inorganic and organic molecules into a 3D network using 3D molecular deposition. In our previous works, we have demonstrated the ability to link inorganic and organic molecules into a 3D nanostructure using the ALD/MLD thin-film technique.²⁹ Unlike earlier deposition techniques, this technique allows consecutive deposition of individual inorganic and organic molecular layers to create 3D films of precise nanothickness.

Here, inspired by the 2D supramolecular networks construction on surfaces and following our recent progress in developing novel crystalline inorganic-organic architectures utilizing the emerging ALD/MLD thin-film technique,³⁰⁻³² we present in this work a new type of 3D inorganic-organic hybrid structure based on a nucleic acid (uracil) as the organic component and sodium as the metal linker. Based on comprehensive structural characterization and computational calculations we propose a possible structure for our Na-uracil hybrid thin films, and demonstrate that such sodium-mediated 3D uracil network may possess luminescence properties different from those seen for molecular uracil. Moreover, owing to the unique deposition mode of the ALD/MLD technique^{29,33,34} based on successive self-saturative gas-solid reactions of separately introduced gaseous precursor pulses, the ALD/MLD grown hybrid thin films possess in general a number of attractive properties such as a precisely controlled film thickness, large-area homogeneity and excellent conformity even over the most demanding surfaces such as nanostructured, sensitive or flexible substrates.

Experimental

The Na-uracil thin films were grown using in-house made Na(thd) (thd: 2,2,6,6-tetramethyl-3,5-heptadionate)³⁵ and commercial uracil powder (Sigma Aldrich) as precursors; the precursor powders were sublimed from glass crucibles which were kept inside the reactor, at 195 and 235 °C, respectively. Nitrogen (99.999 %); Schmidlin UHPN 3000 N₂ generator) was used as a carrier and purging gas, and a pressure of 2-4 mbar was maintained in the reactor during the film deposition. The following sequence of pulses (*i.e.* the ALD/MLD cycle) was continuously repeated $n = 200$ times: $n \times [\text{Na(thd)} \text{ 1.5 s} \rightarrow \text{N}_2 \text{ purge 2 s} \rightarrow \text{uracil 2 s} \rightarrow \text{N}_2 \text{ purge 4 s}]$. The depositions were carried out in a commercial ALD reactor (F-120 by ASM Microchemistry Ltd) at 300 °C on Si(100) substrates cut into 3.5 x 3.5 cm² pieces; the substrates were used as received. The film thickness was determined from the cantilever tip jump in the atomic force microscope (AFM; TopoMetrix Explorer). For

the thickness measurement, fine scratch marks were created with a sharp scalpel blade to find a step corresponding to the thickness of the film. After that the AFM tip was scanned along the edge of the scratch mark. The AFM tip jump corresponds to the thickness of the film. The thickness of the film was estimated from the AFM data using the Gwyddion surface microscopy software.³⁶ Grazing incidence X-ray diffraction measurements (GIXRD; PanAnalytical Pert MPD Pro Alfa X-ray diffractometer; Cu-K α radiation) were performed to investigate the crystallinity of the films. Fourier transform infrared measurements (FTIR; Nicolet 380 spectrometer (Thermo Fisher Scientific) were carried out in transmission mode with a 1 cm⁻¹ resolution and averaged over a minimum of 64 scans. ¹H nuclear magnetic resonance spectra (NMR; Bruker Avance 400 spectrometer) were recorded at room temperature; scale was calibrated to internal reference tetramethylsilane (TMS). X-ray photoelectron spectra (XPS; Kratos Axis Ultra spectrometer; monochromated Al-K α radiation and charge neutralization) were measured for both the thin films and the uracil precursor using a pass energy of 20 eV, an X-ray power of 75 W and an analysis area of approximately 700 x 300 μm^2 . The nitrogen 1s peak of uracil at 400.9 eV was used as a reference to correct for the sample charging.

Optical properties were investigated through UV-Vis absorption (Perkin Elmer Lambda 950 UV/Vis/NIR absorption spectrophotometer) and fluorescence spectroscopy (Quanta Master 40 spectrofluorometer, Photon Technology International) measurements. The time-resolved measurements were performed using a frequency-doubled, mode-locked Ti:S laser (Coherent, Mira 900-F, rep. rate 76 MHz, pulse width 200 fs) as the excitation source. The fluorescence decay was collected with a Peltier cooled microchannel plate photomultiplier tube (MCP-PMT, Hamamatsu) and single photon counting electronics (BH).

Results and discussion

Our Na(thd)+uracil ALD/MLD process yielded visually homogeneous and stable thin films. Based on the ALD/MLD,²⁹ we may assume that Na(thd) reacts through ligand-exchange reactions with uracil to form the Na-uracil thin film in an atomic/molecular layer-by-layer manner. For the film grown with 200 ALD/MLD cycles the film thickness was 95 ± 5 nm determined from the cantilever tip jump in the AFM height profile as shown in Fig. 2. From this film thickness value, the growth-per-cycle (GPC) rate could be calculated at $4.8 \text{ \AA/cycle}$. From the GIXRD measurements, the as-deposited films could be confirmed to be crystalline with sharp diffraction peaks indicating a substantially high degree of crystallinity, see Fig. 3. However, we could not match the diffraction peaks to any known crystal structure; this was rather expected as the Na-uracil materials realized here through the ALD/MLD technique are believed to be fundamentally new types of nucleic acid-derived hybrid materials.

Figure 2: Thickness measured by AFM of Na-uracil thin film sample deposited with 200 ALD/MLD cycles.

Figure 3: GIXRD pattern for Na-uracil thin-film sample.

From Fig. 4 can be seen the FTIR spectrum for the same Na-uracil thin-film sample together with a spectrum for the uracil powder employed as the precursor in our thin-film depositions. The features seen for the uracil reference are well explained based on the literature data: the absorptions due to the N-H, C-H and O-H bonds are seen in the area $2820\text{--}3081\text{ cm}^{-1}$, the C=C and C=O bonds in the area $1550\text{--}1750\text{ cm}^{-1}$ and the N-H bonds in the area $1350\text{--}1550\text{ cm}^{-1}$.³⁷ In particular, the bending vibration N1-H is seen at 1507 cm^{-1} and the N3-H vibration at 1414 cm^{-1} .³⁸ Also, from previous works it is known that Na has a tendency to bind to the uracil molecule via O atoms.³⁹ Fig. 4 shows that upon the ALD/MLD thin film growth the feature due to $\nu(\text{C2=O})$ at 1710 cm^{-1} shifts towards the lower frequency (1699 cm^{-1}) and the feature due to $\nu(\text{C4=O})+\nu(\text{C=C})$ at 1675 cm^{-1} disappears, while the third strong band observed at 1630 cm^{-1} for uracil moves to the lower frequency (1608 cm^{-1}), which indicates that the C=O group is indeed involved in the coordination of Na atoms in our Na-uracil thin-film material.^{40–42}

Not only the shifts of the aforementioned features to the lower frequencies but also the shifts in the range of $750\text{--}820\text{ cm}^{-1}$ are related to the displacement of the H5 proton in uracil due to an adjacent Na atom.⁴³

From Fig. 4 can be seen that the bending vibration seen at 1414 cm^{-1} for uracil shifts to the higher frequency for the Na-uracil thin film (1427 cm^{-1}). A similar increase in frequency

Figure 4: FTIR spectra for the reference uracil powder (red, top) and our Na-uracil thin film (blue, bottom).

has been previously reported for uracil N3-H coupled with C=O.⁴² Another observation is that the $\sigma(\text{N1-H})$ vibration at 1507 cm^{-1} shifts to the higher frequency (1553 cm^{-1}), indicating that N1-H...O hydrogen bond pairs are formed between uracil molecules.⁴⁴ This new intense band at 1553 cm^{-1} has also been assigned to the vibration of the O-C-N-C-O moiety where the deprotonated nitrogen is coupled to a metal.^{45,46}

Further the diminished frequency of $\nu(\text{N-H})$ from 3129 to 2918 cm^{-1} shows that there is involvement of the N-H groups in the Na-uracil 3D lattice formation through hydrogen bonds. Also, it is very well known that the O-H and N-H stretching peaks are usually broadened by hydrogen bonds; hence the broad absorption band seen between 2700 and 3100 cm^{-1} for the Na-uracil thin film is most likely the OH portion broadened by hydrogen bonding.⁴⁷ The most significant red shifts are observed for the modes of $\nu(\text{N3-H})$ from 3129 to 2918 cm^{-1} and of $\nu(\text{C=O})$ from 1710 to 1699 cm^{-1} , indicating that N3-H and C=O indeed are involved in strong hydrogen bonds.⁴⁸

In Fig. 5 we display the ^1H NMR spectra for both the uracil powder and our Na-uracil thin film; the data are well in line with the interpretations made based on the FTIR data. From the NMR spectra it can be seen that upon the ALD/MLD process the greatest fraction of protons originally present in uracil are lost from the N1-H and N3-H sites; the nearly complete disappearance of both the amino proton signals gives evidence of their

participation in the Na-uracil film formation.⁴⁹ Most likely the broad peak found between 9 and 10 ppm in the Na-uracil spectrum indicates that resonances N1-H and N3-H are in the interaction with oxygen and involved in the hydrogen bond formation through the O-H group (N-H...O).⁵⁰ Furthermore, the NMR spectra show clearly that the H5 signal is slightly up-field shifted upon the charge redistribution in Na-uracil, while the H6 protons are hardly affected (up-field shift 0.02 ppm).

Figure 5: ^1H NMR spectra for uracil (red, top) and Na-uracil (blue, bottom) measured in dry d_6 -DMSO.

We also measured XPS spectra of the N 1s, C 1s, Na 1s and O 1s regions for both our Na-uracil thin film and the uracil reference sample, see Fig. 6. For pure uracil the spectra are essentially equivalent to those previously reported in literature.⁵¹ The two inequivalent nitrogen atoms, N1 and N3, are observed as one peak at 400.9 ± 0.1 eV and the two inequivalent oxygen atoms as one peak at 532.0 ± 0.1 eV. The different carbon atoms on the other hand are resolved in the C 1s spectrum: the component at 285.1 ± 0.1 eV (C5) appears somewhat more pronounced than the others since it contains also an overlapping contribution from hydrocarbon contamination of the sample.

For our Na-uracil thin film a clear Na 1s peak is observed at 1072.3 ± 0.1 eV; this fits to a number of different types of Na bonding, including bonding with oxygen.⁵² The O 1s peak is found at 531.9 ± 0.1 eV, *i.e.* essentially at the same energy as in the uracil reference. Most notably, an additional N peak is observed at 399.1 ± 0.1 eV for the Na-uracil thin film. We

Figure 6: XPS spectra of N 1s, C 1s, Na 1s and O 1s regions for uracil powder (red/top curves) and our Na-uracil thin film (blue/bottom curves).

assign this feature to deprotonation of a N atom in the uracil molecule,^{24,53} which should cause changes in the Na-uracil C 1s spectrum as well. For example if N3 were deprotonated, shifts of ca. - 1 eV for the binding energies of C2 and C4 should be expected.^{24,53} In the C 1s spectrum for Na-uracil, clearly, such large shifts are not observed, but the peak positions and/or area ratios of C2 and C4 show small changes only. This would be expected if for example only a portion of the uracil molecules would undergo the deprotonation. Atomic concentrations calculated from the peak areas for the two samples can be found in Table S1 (in Supporting Information). No other elements than those expected were found (see the survey spectra (Fig. S12) in Supporting Information). The concentrations for uracil are rather stoichiometric, but the Na-uracil thin film clearly deviates from this. The O and Na concentrations are quite high whereas the N and C concentrations are lower than in the reference uracil sample. The crystalline nature of our Na-uracil thin film has to be taken into account since the XPS signal is strongly surface sensitive. The results could imply that the molecular layer grows in a non-planar fashion with the O atoms closest to the surface. If we assume that Na is bonded to one of the O atoms then this would also explain the high Na content on the surface. As a consequence the amount of deprotonated N would also be overestimated if calculated from the area ratio of the two N peaks observed.

Since the GIXRD peaks did not match to any known crystal structure, and it was not possible to solve the new crystal structure based on the peaks observed for presumably polycrystalline thin films, we performed an exploration of the geometrical parameters of periodic Na-uracil compounds using density functional theory (DFT) at the generalized gradient correction level within a real-space projected augmented wave-function formalism as implemented in GPAW code.⁵⁴ In all calculations the TS09 pair-wise van der Waals (vdW) correction⁵⁵ was included to improve the accuracy of the results.²¹ It is worth to mention that the inclusion of the vdW correction is extremely important to obtain a stable layered structure, only with PBE⁵⁶ without correction the planes are not stable to form a crystal. Our methodology uses a bottom-up approach to predict energetically favorable configurations using the experimental results as a guide. Details of the computational methodology are found in Supporting Information. The formation of one specific crystal phase in the uracil compounds stabilized through hydrogen bonds and stacking interactions is a well-known result.^{57,58} However, the inclusion of the metal ion, *i.e.* Na^+ , in a stable structure is a novel and challenging result.

The single uracil- Na^+ unit has an energy binding at PBE-TS09 level of 37.4 kcal/mol in the O4 position, and around 4 kcal/mol less at the O2 site (see Supporting information). The possibility of protonation upon ensemble of pure uracil supramolecular structures has been observed at experimental level on copper surfaces,²⁴ where the N3 position turns into the main hydrogen donor. In our study we evaluated all the different binding possibilities in order to find the structure that predicts best the 3D thin-film formation of the Na-uracil compound. It is important to highlight that from computational calculations, the most stable configuration upon protonation of N in the single uracil- Na^+ unit is the structure with a double bond towards the O2 and N3 atoms (see Supporting Information). However there is not conclusive experimental evidence of this double bonded interaction in the structure and the combined FTIR and XPS data show a clear O2- Na^+ interaction. The XPS data actually showed the presence of two types of N atoms in the thin-film sample. The metal-organic

expected bond from XPS data is therefore O2- Na^+ with protonated N3 uracil that has an energy binding at PBE-TS09 level of 120.61 kcal/mol.

Previous studies have shown that crystallization in tetrameric-like structures are favorable for nucleic acids.⁵⁹ A tetrameric configuration also allows the generation of 2D periodic structures that can be themselves stable prior the cation addition. We have in the following restricted our exploration to tetrameric structures, *i.e.* to planar structures where three neutral uracil molecules stabilized through hydrogen bonds interact with one protonated uracil then fully neutralized upon addition of one Na^+ cation in the central space, see Fig. 7.

Figure 7: Representation of the proposed tetrameric uracil/sodium structure. The respective hydrogen bonds are depicted with points. Note that all the O2-H1' distances are different (but still in the range of one hydrogen bond). The Na^+ ion appears at the center of the tetramer (in magenta) with the shortest distance towards the protonated uracil.

We find that the most stable planar tetrameric structure is stabilized through hydrogen bonds between the O2-H1' centers of two consecutive uracil and the ionic bonding with the Na^+ cation, which is coordinated with the four O2 atoms from each uracil. The O2-H1' distances are different due to the asymmetry introduced by the deprotonation of one of the uracils being from the shortest to the largest: 1.51, 1.7, 1.93 and 2.44 Å. The Na-O distances are similar among the neutral uracils being 2.39 Å in average and 2.17 Å with the deprotonated uracil. The experimentally determined high density of hydrogen bonds (N3-H and N1-H) also supports the choice of the tetrameric configuration. In addition, the

^1H -NMR data showed that the C5 atom slightly up-field shifts upon the charge redistribution during the Na-uracil thin-film formation that is in agreement with our model. Concerning a possible extension to the infinite plane, our calculations using a geometrical minimization algorithm show that the tetrameric symmetry is highly stable after a slight distortion of the planarity (see Supporting Information).

Finally, after the structural characterization of Na-uracil thin films we were motivated to investigate the optical properties of the new material. Firstly, we measured the absorption spectra for both the uracil reference and a Na-uracil thin film deposited on quartz, see Fig. 8. The uracil reference sample shows the characteristic absorption peaks at ca. 200 and 260 nm, which are usually assigned in literature as the n/π^* and π/π^* transitions, respectively.⁶⁰ From Fig. 8, for the Na-uracil thin film a bathochromic shift for both the peaks is seen, being more pronounced for the shift of the 260 nm peak towards the red wavelengths. In addition, the 260 nm peak is broadened and shows a long spectral trail extending to the visible wavelength range. A very similar spectral behavior has been observed for push-pull purines upon the introduction of suitable electron donor and acceptor groups that also exhibited enhanced luminescence.^{17,61,62} However, in our case the situation is more complex. The broadening and the spectral trail could be explained by the structural heterogeneity of the uracil-sodium assembly, which would lead to various energetically different associated species. This heterogeneity leads to the broadening of the absorption spectra and could give rise to the spectral trail at long wavelengths. Moreover, these effects are more pronounced in assemblies that include hydrogen bonds and electrostatic interactions.^{63–66} The bathochromic shift of the 260 nm absorption peak could originate from the uracil head-to-tail configuration as predicted by the exciton model by Kasha *et al.*⁶⁷ The head-to-tail configuration of uracil molecules is supported by our DFT calculations that demonstrate a periodic structure formed by the uracil and sodium in planar tetrameric configuration.

Figure 8: Absorption spectra for our Na-uracil the deposited uracil and complexes on quartz, inset shows uracil visualized under UV light (left). Fluorescence spectra for the Na-uracil thin film with 280 and 400 nm excitation (right).

Secondly, we carried out steady-state fluorescence measurements; Fig. 8 shows the fairly strong and bright fluorescence spectra taken at excitation wavelengths of 280 and 400 nm. The bright fluorescence signal for the 400 nm excitation is not commonly observed for uracil compounds due to the low quantum yields of purines and pyrimidines in gas or aqueous phase.^{60,68,69} In addition, the fluorescence spectra interestingly exhibit a substantial red shift between the pump wavelengths of 280 and 400 nm, which in itself is a rare phenomenon in organic fluorescing materials.⁷⁰ However, this effect is beyond the scope of this study and will be investigated in more detail later. Nevertheless, these exceptional fluorescence properties of our Na-uracil thin film motivated us to investigate if these effects would be reflected in the lifetimes. The lifetime from the time-resolved decay was analyzed using a two-exponential model as previously described.⁷¹ Typically, the lifetimes for nucleic acids in aqueous solution are in the order of picoseconds, which is a result of extremely efficient internal conversion.⁷² However, the observed lifetime for our samples is 1.9 ns measured at the emission wavelength of 460 nm using a 400 nm excitation, which is approximately three orders of magnitude higher than values earlier reported for uracil.^{72,73} The lifetime can be defined as $\tau = (\Gamma + k_{\text{nr}})^{-1}$, where Γ is the radiative decay rate and k_{nr} is the nonradiative decay rate. Hence, to explain the observed increase in the lifetime, one of the rate constants must decrease. In this case, the

most probable option would be that the extensive hydrogen bonding network between uracil molecules and the interactions between uracil and sodium inhibit the internal conversion process that ultimately leads to the decrease in the nonradiative decay rate. This conclusion would also be in accordance with the observed strong and bright fluorescence in our steady-state measurements.

Conclusion

We have demonstrated the exciting new possibility to link nucleic acid (here uracil) molecules and metal (here sodium) atoms into fundamentally new type of crystalline 3D network using the currently strongly emerging ALD/MLD thin-film technology. We propose a tetrametric symmetry stabilized through hydrogen bonds and the Na cation as a feasible structure for the films. Also interestingly, it was shown that the Na-uracil network exhibited significantly different optical properties from those seen for isolated uracil molecules. We foresee that our approach will generate a rich multitude of new ideas for the smart design of novel nucleic acid-derived assemblies.

Supporting Information Available

- Computational modeling
- XPS

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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