

[1], [2].

A sequence of bidimensional X-ray diffraction patterns were acquired in transmission mode at regular intervals across the shell thickness. The scattering or degree of preferential orientation of crystals was calculated from the intensity profile along the selected Debye-Scherrer rings (χ -scans).

The degree of crystal orientation was determined from the angular length of the arcs displayed in the Debye rings on the 2D X-ray diffraction patterns. The values of reflection intensities, degree of orientation and crystallinity show progressive variations within during the same shell layer as well as abrupt changes at the transitions between layers with different microstructural organizations. This study provides useful insights into both the mechanisms that control the development of order in mollusc shell microstructures and those that determine the switch between layers with different microstructural organizations.

This information could be of interest to understand the processes of self-assembly that happen in these biomaterials and may be applied to the design of bio-inspired advanced ceramic materials.

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Keywords: mollusk shell, crystallographic orientation, X-ray diffraction

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Oriented nucleation of hemozoin at the food vacuole membrane in *P. falciparum*

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The nucleation of hemozoin (HZ) in the digestive vacuole (DV) of *Plasmodium falciparum* in malaria-infected red blood cells (RBCs) is a topic of current interest. HZ crystals have been reported encased within neutral lipid nanospheres in the DV, which appears inconsistent with the concepts of catalyzed nucleation of HZ at a lipid surface and inhibition of nucleation of HZ via antimalarials that target the HZ crystal surface. To resolve this conundrum, we probed the orientation of HZ crystals in the DV, their position, the site and mechanism of nucleation. HZ crystal clusters in the RBCs were detected and their amount estimated by microfocus X-ray Fe-fluorescence, and their orientations determined by microfocus X-ray diffraction. The diffraction patterns were interpreted in terms of HZ crystals aligned along their needle axes, arranged on a curved surface, exposing their {100} side faces. Using various microscopy techniques, including stain-free cryogenic soft X-ray tomography, freeze-fracture SEM and thin section TEM, we find that nucleation occurs in proximity to the DV inner membrane, where furthermore we find a thickened lipid coating. Morphological evidence supports the {100} orientation facing the lipid, consistent with interpretation of X-ray diffraction results (mentioned above) and *in vitro* nucleation of synthetic hemozoin at various interfaces.

Keywords: biomineralization, malaria, hemozoin

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Single crystal growth and characterization of lead hydroxyapatite

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Calcium hydroxyapatite (CaHAP, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) is the dominant component of human enamel, dentin, and bone. Its structure belongs to space group $P6_3/m$ and is susceptible to ionic substitution in both anion and cation sites. Pb^{2+} can replace Ca^{2+} in the apatite structure resulting in lead hydroxyapatite (PbHAP) which is isostructural with CaHAP. This work reports products from a gel crystallization method used for preparation of larger crystals of PbHAP by controlling nucleation and crystal growth rate by changing the density of the gel medium. Crystals obtained in milli-scale on top of the gel exhibit equant morphology while crystals inside the gel layer exhibit pennant morphology. FT-IR spectra of the products exhibit asymmetric (PO) stretching, symmetric (PO) stretching, and (OPO) bending in the 1002-1047 cm^{-1} , 924-956 cm^{-1} , and 518-600 cm^{-1} regions, respectively, and OH stretching at 3555 cm^{-1} . The FT-IR spectrum of the product on top of the gel also showed NO_3^- bands (NO_3^- from lead nitrate starting material) which are not present in the product formed inside the gel layer.

Keywords: hydroxyapatite, apatite, gel crystallization

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Self-assembly of metallated TPP porphyrin by external dipyrindyl ligands

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Supramolecular entities based on self-assembly of metalloporphyrins are paradigmatic examples of the great efficiency of the nanodevices used by natural systems in photosynthesis, oxygen transport, electron transfer and catalysis [1]. Therefore, they constitute reference models for the development of new materials that make these, and other yet unexplored, functions.

While metalloporphyrin biosystems operate in solution, the preparation of materials based on these macrocycles moves the problem to the solid state synthesis. Thus, obtaining supramolecular entities may be approached by different strategies of synthetic design. One of them consists on the use of external dipyrindyl ligands to assemble the metallated porphyrin units. In this aspect, the range of compounds that can be used is endless. In this context, our research group is working with different combinations of organic ligands and metalloporphyrins, and the work herein presented corresponds to the compound [FeTPP(bipy)] (TPP=meso-tetraphenylporphyrin and bipy=4,4'-bipyridine), obtained by solvothermal synthesis.

The crystal structure of [FeTPP(bipy)] consists of 1D chains of alternating FeTPP and bipy molecules bonded to the axial positions of the coordination sphere. These chains are sustained by π - π stacking between the phenyl rings at about 5 Å.

So far, very few compounds with TPP and bipy have been described, of which only one [2] is really a 1D coordination polymer, being all others isolated dimers. It is also remarkable that, as far as we know,