

source was used and the sample located relatively far away in order to obtain mild coating conditions.

Device characterization was performed under nitrogen atmosphere in the forward-bias configuration (with ITO positive); the emitted light was detected through the transparent ITO electrode and substrate. The EL intensity was measured using a calibrated silicon photodiode and a Keithley 617 Electrometer, while the current-voltage (I - V) curves using a Keithley 230 Voltage Source and a Keithley 2001 digital multimeter. PL and EL spectra were recorded by a Perkin Elmer LS-50 spectrophotometer. All the measurements were performed at room temperature.

Received: July 5, 1996

Final version: September 20, 1996

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Template-Directed Synthesis of Aragonite Under Supramolecular Hydrogen-Bonded Langmuir Monolayers**

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The calcium carbonate polymorph aragonite (CaCO_3) is metastable under ambient conditions, yet it is found as a natural component in fish otoliths,^[1,2] human brain

stones,^[3] gallstones,^[4] and, notably, in the nacreous layer of mollusc shells.^[1,2] This structural selectivity has long been an intriguing aspect of biomineralization, and recent studies suggest that specific biological macromolecules are involved in controlling aragonite nucleation.^[5,6] In comparison, the laboratory synthesis of aragonite from supersaturated solutions at room temperature has not been achieved without the use of soluble additives such as Mg^{2+} or small organic molecules.^[7,8] Here, we demonstrate that the spreading of 5-hexadecyloxyisophthalic acid (C_{16}ISA) at the air/water interface results in the specific nucleation of aragonite from supersaturated calcium bicarbonate solution not doped with additives. We show that the [010] axis of aragonite is preferentially aligned perpendicular to the monolayer surface and suggest that a close structural correspondence between the ac face of aragonite and the hydrogen-bonded network of the self-assembled template is responsible for interfacial molecular recognition at the organic/inorganic interface during crystallization. The results illustrate the possibility of designing supramolecular templates to direct the synthesis of organized inorganic materials.

The template-directed nucleation of inorganic materials by organic supramolecular frameworks is an overarching principle in biomineralization. Nacre biomineralization, for example, is a highly controlled process that involves oriented nucleation, growth and organization of plate-like aragonite crystals within a complex organic matrix.^[9,10]

The ability of organized organic surfaces to induce oriented inorganic nucleation and polymorph selectivity has been modelled by investigations of calcium carbonate crystallization under Langmuir monolayers.^[11-14] These studies clearly showed that oriented nucleation either calcite or vaterite is dependent on the structural and chemical properties of the monomolecular films. However, none of the surfactants studied to date selectively induced nucleation of aragonite unless Mg^{2+} ions are introduced into the supersaturated subphase.^[7]

Scanning electron microscopy (SEM) micrographs of the CaCO_3 crystals grown under compressed C_{16}ISA monolayers (Fig. 1) showed discrete 100 μm bundles of aragonite needles that developed from a central crystallite which was in direct contact with the monolayer surface. The primary crystals grew to approximately 10 μm in size before secondary nucleation of the crystalline needles gave rise to a splayed outgrowth into the supersaturated solution. The early stages of crystal growth were investigated by studying samples extracted after 5–15 min of crystallization at the monolayer/subphase interface. Transmission electron microscopy (TEM) micrographs showed incipient crystals as hexagonal tablets with roughened edges (Fig. 2). Selected area electron diffraction patterns recorded from individual particles suggested that the nucleated aragonite crystals were oriented with the [010] crystallographic axis perpendicular to the monolayer surface (Fig. 2). The data suggest that aragonite is nucleated specifically from the ac crystal face.

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[**] We thank S. Weiner and L. Addadi for their critical review of this manuscript and E. Bruno and J. M. Didymus for technical assistance. We are grateful to C. Sung for TEM and V. Tsukruk and V. Bliznyuk for AFM support.

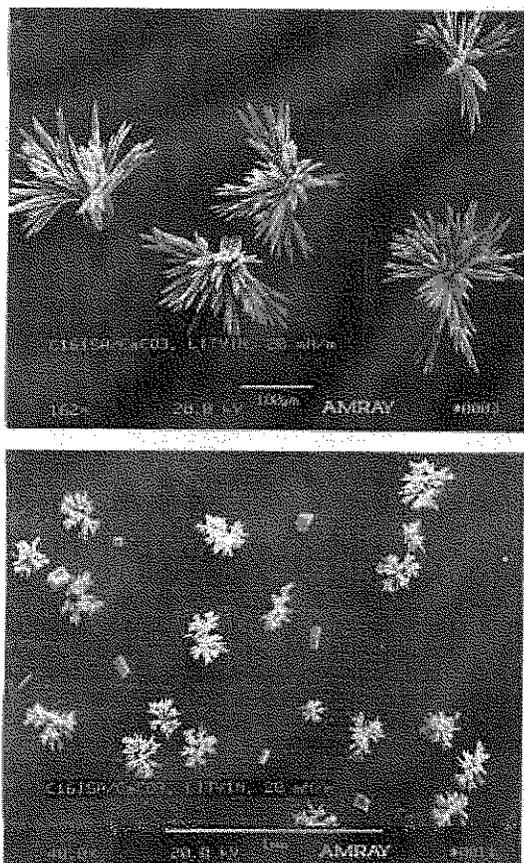


Fig. 1. SEM image of aragonite crystals grown under a C_{16} ISA monolayer. Crystals were deposited on aluminum SEM stubs by dipping through the monolayer/subphase interface. The view shown corresponds to a direction from below the monolayer. Calcite crystals with an unmodified rhombohedral habit are also observed. The stubs were coated with a thin layer of gold (about 100 Å) under vacuum to minimize charge on the samples. Scale bar = 100 μm (top) and 1 mm (bottom).

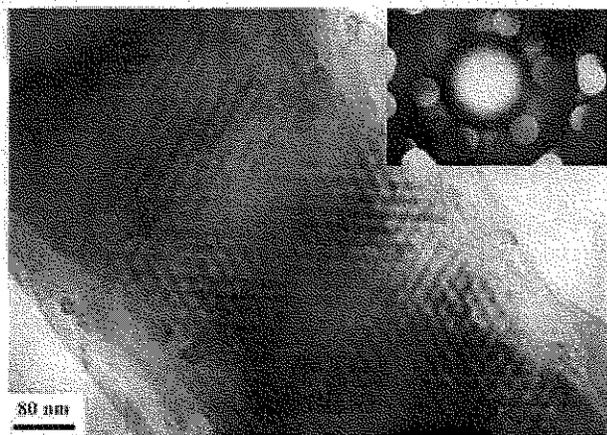


Fig. 2. TEM micrograph of an immature aragonite crystal nucleated under compressed C_{16} ISA monolayer ($t = 7$ min). The scale bar = 80 nm. Inset shows electron diffraction pattern of crystal imaged above. The pattern corresponds to the [010] zone of aragonite. Reflections: $A = 102$ (2.48 Å), $B = 10\bar{2}$ (2.48 Å), $C = 200$ (2.48 Å). Angles: $(102) \wedge (10\bar{2}) = 119.9^\circ$; $(102) \wedge (200) = 59.95^\circ$. Crystal structure of aragonite, $Pmcn(62)$, $a = 4.96$, $b = 7.967$, $c = 5.74$ Å. A Philips EM4001 TEM was used for low and high resolution imaging. Individual crystals were studied by convergent beam electron diffraction.

To clarify the role of the C_{16} ISA template in aragonite nucleation, we built a model for the Langmuir monolayer, based on experimental evidence from X-ray crystallography,^[15] Fourier transform infrared (FTIR) spectroscopy, and atomic force microscopy (AFM). FTIR was used to investigate hydrogen-bonding in the C_{16} ISA monolayer. The monolayer was deposited on ZnSe substrates from either water or calcium bicarbonate subphases. In both cases, broad bands from the OH-groups were observed at 2650 cm^{-1} , which indicate hydrogen bonding between the adjacent carboxylic acid groups and water^[16] (data not shown). We constructed our C_{16} ISA monolayer model based on the crystal structures of C_{12} ISA \cdot EtOH^[15] and C_{14} ISA \cdot H₂O. In our model each molecule resides in a rectangular lattice and interacts with two neighbors through hydrogen bonding along the c -direction and a further two molecules via van der Waals forces along the a -direction (Fig. 3). The AFM images showed that the arrangement of C_{16} ISA molecules within a monolayer resulted in periodic domains of carboxyl groups spaced at 4.4 and 5.5 Å along the a - and c -directions, respectively (Figs. 3 and 4). These measurements are in good agreement with synchrotron X-ray diffraction studies of monolayers of a long-chain alkyl surfactant with an aromatic headgroup^[17] and with the stacking of flat aromatic organic molecules within three-dimensional crystals (4.7 Å).^[18]

Surface pressure–area isotherms for C_{16} ISA monolayers compressed on either water or calcium bicarbonate solutions were identical (data not shown). Similarly, Brewster angle microscopy data also showed that self-assembly of the C_{16} ISA monolayers was not influenced by Ca^{2+} ions in the subphase (data not shown). These results, although contrary to previous work on other surfactant monolayers in which significant increase in area per molecule ($\sim 4.5\text{--}5\text{ \AA}^2$) were recorded in the presence of Ca^{2+} -containing subphases,^[14] indicate that the structural network of the C_{16} ISA monolayer is preorganized. The main reason for this is probably due to the significant cross-sectional mismatch between head and tail regions of the C_{16} ISA molecule. The head groups occupy a relatively large molecular area in the packed array, such that Ca^{2+} ions can be accommodated without significant changes in intermolecular distances (4.4 and 5.5 Å). At least two binding models are plausible: firstly, carboxylate groups of individual molecules form double-chelate complexes with Ca^{2+} ions,^[19] or secondly, a bridging mode in which Ca^{2+} ions interact with carboxylate groups of different molecules.^[20] In both cases, our model gives a close match between the experimental parameters of the C_{16} ISA template and Ca–Ca distances and angles in the ac plane of aragonite (Fig. 3), suggesting that geometric correspondence is important in determining polymorph selectivity. A further possibility is that the bidentate motif of the meta-disposed carboxylates complements the stereochemical arrangement of the carbonate anions in the ac -face. In this regard, we note that in the presence of Mg^{2+} ions, long-chain alkyl sulfate or phosphonate monolayers

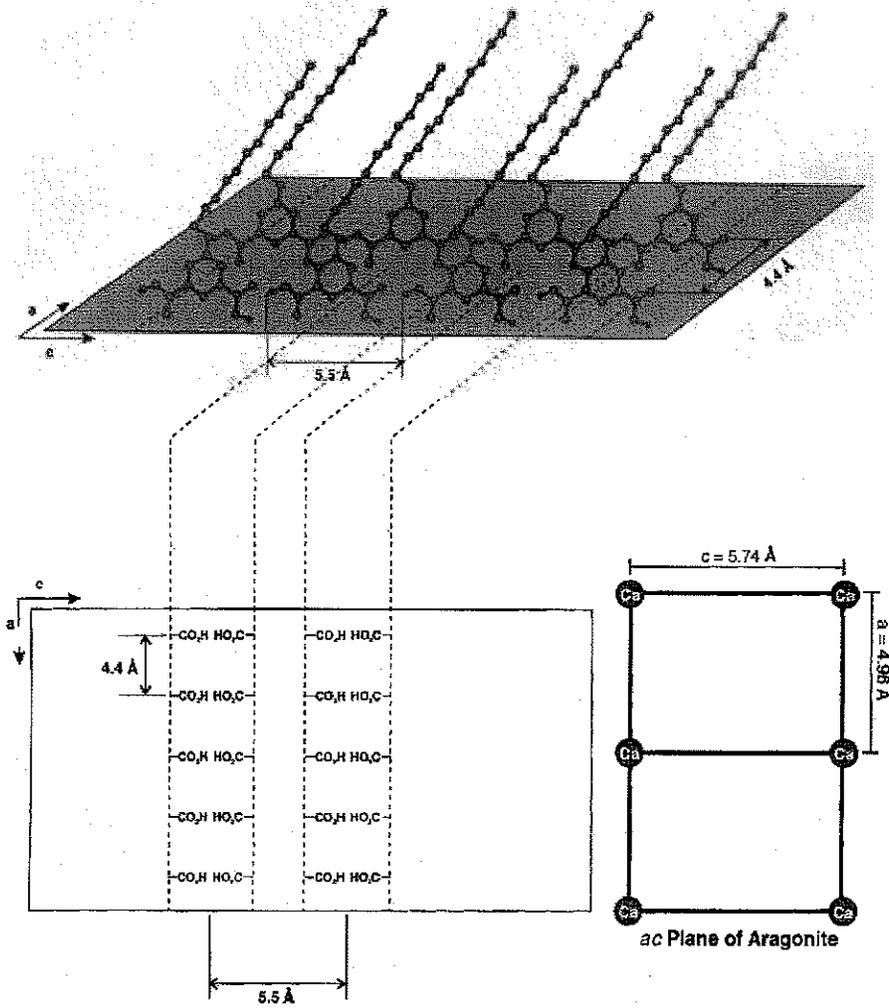


Fig. 3. Schematic representation of the spatial relationship between a periodic C_{16}ISA monolayer and the ac -plane of aragonite.

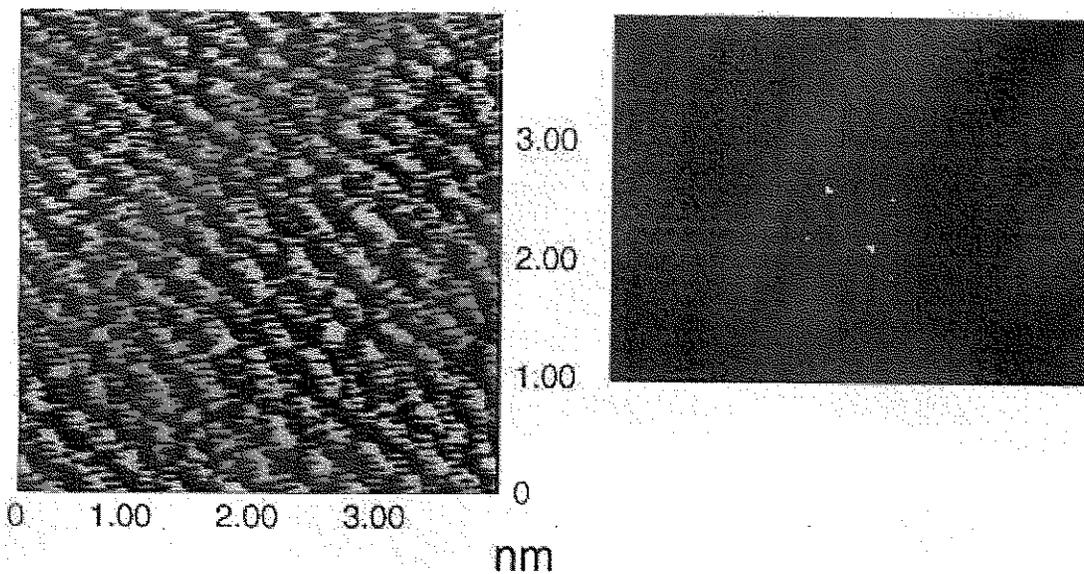


Fig. 4. AFM image at atomic resolution of a C_{16}ISA monolayer deposited at 10 mN/m on hydrophilic silicon surface (top). Fourier transform image of the monolayer imaged above (bottom).

induce nucleation of the (001) (*ab*) face of aragonite,^[7] possibly by correspondence between the tridentate headgroup and planar carbonates of this face.

Finally, we note that the C₁₆ISA monolayer functions in an analogous manner to the β -pleated sheet matrix of nacre biomineralization. In both cases, the supramolecular organization is produced by hydrogen bonding and the surface periodicities are commensurate with Ca–Ca distances in the specific crystal faces of aragonite. A laboratory analogue based on biomimetic principles provides an opportunity to improve our understanding of alternative synthetic pathways to the controlled formation of inorganic materials with selected polymorph structures.

In summary, it has been demonstrated that aragonite can be selectively nucleated without the use of additives. This result strongly supports the concept that functionalization and supramolecular organization play a key synergistic role in controlled crystallization in biological and synthetic systems.

Experimental

Oriented nucleation of aragonite was achieved by spreading and compressing a Langmuir monolayer of C₁₆ISA on the surface of a supersaturated calcium bicarbonate solution (pH–5.8–6.0, *T* = 21 °C, [Ca²⁺] = 9–9.5 mM). The latter was prepared by purging CO₂ gas for 1 h through a suspension of calcium carbonate in water, followed by filtering and purging again for 0.5 h. We chose C₁₆ISA as the organic template because it was a likely candidate for a hydrogen-bonding network as observed from crystallographic data of C₁₂ISA · EtOH [21]. This network forms due to the presence of the meta-disposed carboxyl groups of the C₁₆ISA benzene rings, and was expected therefore to provide a preorganized supramolecular motif significantly different from the pseudo-hexagonal lattices of conventional surfactants used previously to induce nucleation of inorganic crystals at the monolayer/solution interfaces.

After 12 h, a white sheet of CaCO₃ crystals was visible under the C₁₆ISA monolayer. X-ray diffraction of samples collected from the surface showed that 75–95% of the crystals were aragonite (observed *d*-spacings in Å: 3.40 (111), 3.28 (021), 2.88 (002), 2.74 (121), 2.71 (012), 2.49 (200), 2.41 (031), 2.38 (112), 2.34 (130), 2.33 (022), 2.19 (211), 2.11 (220), 1.98 (221), and 1.88 (202)). In comparison, crystals grown in the absence of the monolayer were predominantly calcite. The specificity for aragonite nucleation was highly sensitive to the structural nature of the monolayers. For example, the highest nucleation density of aragonite (12 ± 3 /mm²) was observed under monolayers compressed within the pressure range 10–15 mN/m. This was consistent with AFM studies, which showed a well-defined uniform C₁₆ISA monolayer deposited on a hydrophilic silicon substrate at this surface pressure. In contrast, broken C₁₆ISA monolayers were deposited at 20 mN/m, although this pressure is well below the collapse point.

Received: August 23, 1996
Final version: October 11, 1996

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Efficient Blue LEDs from a Partially Conjugated Si-Containing PPV Copolymer in a Double-Layer Configuration**

By Frank Garten, Alain Hilberer, Franco Cacialli, Eddy Esselink, Yvonne van Dam, Bart Schlattmann, Richard H. Friend, Teun M. Klapwijk,* and Georges Hadziioannou*

Color tunability towards the blue part of the visible spectrum has proven to be one of the hardest goals to achieve for both organic and inorganic emitters. Although easy tunability in the blue is not a specific peculiarity of organics, cost criteria and the drive to scale-up dimensions of possible applications makes organic blue emitters the focus of technological interest. Electroluminescence (EL)^[1,2] in these (macro)molecular systems can be rationalized in terms of radiative relaxation of π - π^* singlet excitons whose nature depends on the spatial extent of the excited state wavefunction, described by means of the so-called effective conjugation length. In organics, the concept of color tunability towards the blue part of the visible spectrum has so far revolved around the control and limitation of this parameter, for example by choosing short oligomers such as distyrylbenzene,^[3,4] which may be dispersed in a transport

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[**] We thank M. Mulder for technical assistance, and D. Wilms Floet and H.-J. Brouwer for valuable discussions. Financial support from the "Stichting Scheikundig Onderzoek Nederland" (SON) and "Stichting voor de Technische Wetenschappen" (STW), as well as from the HCM program network "Functional materials organized at supramolecular level" is gratefully acknowledged.