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Phase Selection of Calcium Carbonate through the Chirality of Adsorbed Amino Acids**

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Dedicated to Professor Roald Hoffmann on the occasion of his 70th birthday

Chirality and its existence and induction are among the most intriguing and inspiring phenomena in nature.[1] Many explanations have been proposed,[2] one of which focuses on the chiroselective adsorption of amino acids onto chiral mineral surfaces, in particular, on the common rock-forming mineral calcite ($CaCO_3$).[2c] Because the crystal surface lacks the symmetry features of the bulk crystal, the adsorption of an achiral molecule onto a crystal surface may produce chiral 2D arrangements,[3,20] and, vice versa, a chiral molecule on a crystal surface may lead to a chiral entity if ordered 2D adlayers are formed.[4]

Calcite, which is the thermodynamically stable form of the six known calcium carbonate polymorphs, is presumed to have been the most abundant marine mineral in the Archaean era (ca. 3800 to 2500 million years ago). Sumner stated that calcite "precipitated as crystals directly on the sea floor".[2c] Calcite exhibits trigonal symmetry (space group $R\bar{3}c$), and, although this space group contains a center of inversion, calcite surfaces allow enantioselective binding. The typical rhombohedral morphology of calcite is due to the {104} set of crystal planes, which have $P1$ symmetry and are chiral owing to the lack of symmetry elements (Figure 1). The selective binding of different amino acids onto crystal surfaces has been reported for calcium carbonate,[5] as well as for copper[4a–d] and other solids.[4e,f] The chiroselective adsorption of amino acids onto calcite was demonstrated by Hazen et al.,[6] and the formation of chiral morphologies through the selective binding of D- and L-aspartate on growth steps of calcite was studied by DeYoreo and co-workers.[5] These studies provided convincing evidence that the shape of calcite crystals can be modified by binding chiral molecules and thus through stereochemical recognition.

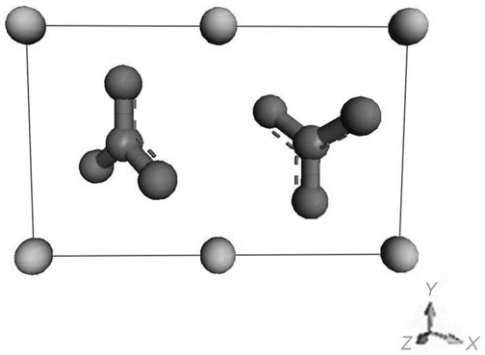

Figure 1. The cleaved (104) surface of calcite shows only the identity symmetry operation.

Stereochemical recognition, which was postulated about two decades ago,[7] is a central tenet in the field of biomineral formation.[8] This postulate states that specific crystal surfaces are stabilized by the binding of molecules such as peptides and proteins because the stereochemical match of the adlayer and the crystal lattice lowers their surface energies.[9] This template model was supported by a series of investigations of the macroscopic shapes of organic or calcium carbonate crystals.[10,11] However, the crystal shape depends not only on surface energy but also on the growth kinetics, and during the past decade a number of elegant studies have related crystal shape to the growth kinetics, which is governed by coordination at kinks and on atomic ledges rather than on the flat faces.[5,12]

Although interactions between the surface and adsorbate are certainly important for the control of crystal morphology, the problem of phase selection is seldom discussed. A well-established example of polymorph selection is the abalone shell, which contains two distinct polymorphs of calcium carbonate;[13] its outer portion consists of calcite, whereas the inner portion (nacre) consists of aragonite. The soluble protein fraction associated with the mineralizing parts of the abalone shell plays a primary role in crystal formation and phase selection.

Although the specific interaction of D/L-aspartic acid with calcium carbonate surfaces has been investigated in some detail,[5,6] most studies addressing stereochemical effects on crystal shape or phase selection disregard chirality. From the

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use of racemic mixtures, it is tacitly assumed that the difference in the interactions of D and L enantiomers on chiral surfaces are small. Herein we demonstrate that the specific interaction between surface and additive chirality is an important factor and does have an important influence on the phase selection of calcium carbonate.

The slow-diffusion technique[14] was used to crystallize calcium carbonate with enantiopure amino acids as additives. In a representative experiment, solutions of both enantiomers of the corresponding amino acids with 10 mM of $CaCl_2$ were placed side by side in the same desiccator for direct comparison. Subsequently, the crystallization process was started by placing ammonium carbonate at the bottom of the desiccator. The crystallization was carried out at 25 °C and was stopped after 48 h. The homogeneous precipitates were collected, carefully washed, dried, and further investigated.

Crystallization experiments were performed with various chiral amino acids (e.g. D/L enantiomers of alanine, proline, α-amino butyric acid, and aspartic acid). The achiral amino acid glycine was used as a reference compound. Scanning electron microscopy (SEM) images of samples precipitated with the D and L enantiomers of the above amino acids are displayed in Figure 2. Alanine, the simplest chiral amino acid, already shows a pronounced effect. In the presence of the natural L form, the dominating phase is vaterite. In contrast, with the D form, only calcite was obtained (Figure 2a, b). Higher nonfunctionalized amino acids lead to the formation of aragonite and calcite; L- and D-proline lead to the crystallization of aragonite, seen as small efflorescent bundles of needles, and calcite (with minor aragonite contamination, as illustrated in Figure 2c, d), respectively. With L- and D-α-amino butyric acid we observed the formation of aragonite and calcite, respectively (Figure 2e, f). The addition of an amino acid bearing higher functionality than a simple α-amino acid reveals a different behavior, for example, cysteine seems to exhibit reverse selectivity. As a comparison, crystallizations with glycine or racemic alanine as additives (under otherwise identical experimental conditions) resulted in mixtures of calcite and aragonite (see the Supporting Information). Glycine and L-alanine are known to stabilize vaterite;[15] however, the conditions chosen herein led to the formation of polymorph mixtures. Amino acids with a higher steric demand, such as trypthophan or tyrosine, do not exhibit phase selectivity as described above.

The phase composition can be determined quantitatively by means of IR spectroscopy, X-ray diffraction, for the evolution of the pH value and the Ca^{2+} concentration in the supernatant, or even by microscopy.

Figure 3 shows the pH profile of the solution during the crystallization in the presence of D- or L-alanine. After the start of the reaction, the pH value of the solution rises within an induction period of about 4 h from below 7 to 8.9 as a result of the dissolution of ammonia that is formed during the decomposition of $(NH_4)_2CO_3$. The better solubility of ammonia relative to that of CO_2 leads to the observed pH change. This equilibrium adjusts during the remainder of the experiment until the NH_3 vapor pressure matches the partial pressure in the gas phase. The continuous formation of

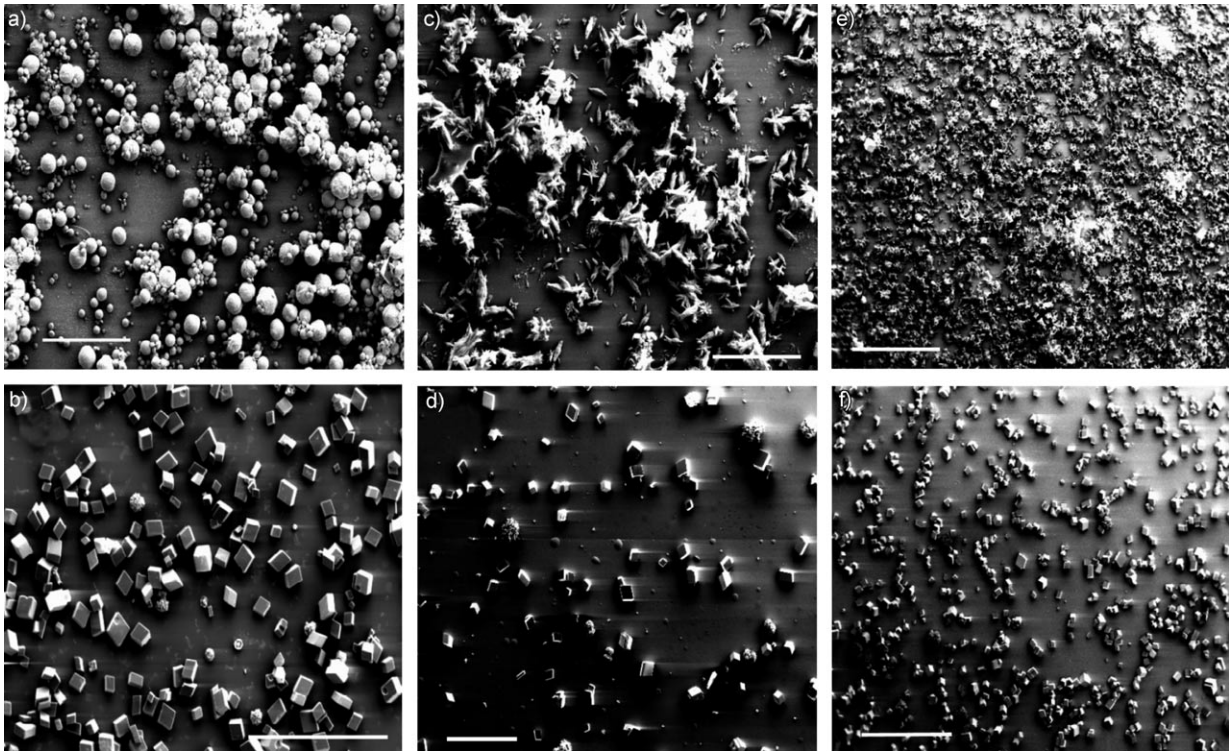

Figure 2. SEM micrographs demonstrating the phase selectivity of the crystallization by addition of L- (a) and D-alanine (b), L- (c) and D-proline (d), and L- (e) and D-α-amino butyric acid (f). Minor calcite contaminations in the case of the L enantiomers are induced by the templating effect of the glass slides. Scale bars: a) 50 μm, b) 200 μm, c) 50 μm, d) 50 μm, e) 500 μm, f) 500 μm.

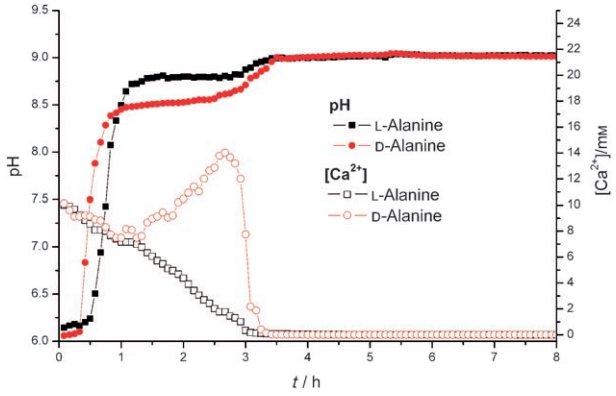

Figure 3. pH value and Ca^{2+} concentration during crystallization with L- and D-alanine as additives.

$CaCO_3$ is indicated by the plateau of the pH value between 1.5 and 3 h, which is caused by the equilibrium of CO_2 uptake and HCO_3^- depletion of the solution as a result of the incipient precipitation of $CaCO_3$. This process releases H^+, which balances the pH rise from the uptake of ammonia. For D-alanine the precipitation occurs earlier. The plateau is reached after a shorter period of time and at a lower pH value. For L-alanine, $CaCO_3$ precipitates later, that is, a higher degree of supersaturation is needed for the nucleation to occur. The progression of the calcium content, monitored by means of a Ca^{2+}-selective electrode,[16] reveals the distinction between both crystallizations containing the two amino acid enantiomers: L-alanine shows a uniform crystallization profile of a steady precipitation leading to the metastable vaterite polymorph (Figure 2a). For D-alanine the precipitation is a two-step process: the already precipitated calcium carbonate redissolves and then subsequently precipitates to give calcite. This step is in harmony with the Ostwald law of stages.

Figure 4 displays the experimental powder XRD patterns corresponding to the material collected from the mineralization experiments with alanine as additive. Relative phase amounts were determined from the relative intensities of reported XRD patterns of the corresponding polymorphs of $CaCO_3$. [17] For the D enantiomer, only calcite was observed,

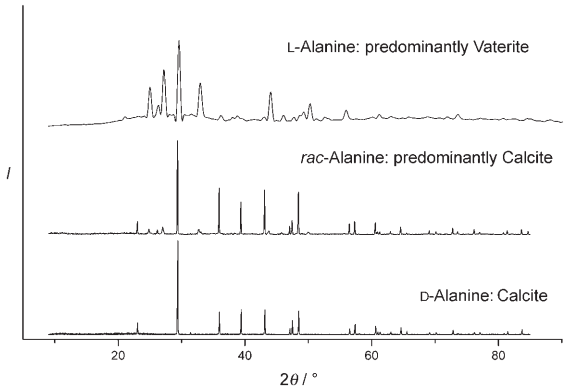

Figure 4. Diffraction patterns of calcium carbonate samples obtained with the addition of 1 mg mL^{-1} L-, D-, or *rac*-alanine.

whereas mainly vaterite was found for the L enantiomer. Such a phase analysis revealed weight fractions of the $CaCO_3$ polymorphs vaterite and calcite in the presence of L-alanine of around 3:1. The results for hydrophilic residues are compiled together with those for glycine in Table 1.

Table 1: Phase distribution (calcite/aragonite/vaterite) for selected amino acids in weight percent.

	Glycine[a]	*rac*-Alanine[b]	Alanine	α-Amino butyric acid	Proline	Valine
L	100/0/0	84/0/16	27/0/73	0/100/0	19/81/0	0/100/0
D			100/0/0	100/0/0	100/0/0	100/0/0

[a] Achiral. [b] Racemic mixture.

The phase selection of calcium carbonate may be rationalized as follows: The growth of the calcite polymorph is prevented by the surface binding of the bidentate amino acid, which attaches more strongly to the growth steps (e.g., $(104) \times (01\bar{4})$) than monocarboxylic acids.[18] Because of the lack of inversion symmetry, the binding motif and therefore the degree of binding is dependent on the chirality of the additive. In case of the L enantiomer, the blockade of the step growth is much more efficient than for the D enantiomer. Therefore, the L enantiomer is able to block calcite and—in the case of the sterically less demanding glycine and alanine—also the growth of aragonite. According to the Ostwald law of stages, the activation barrier of the last step towards calcite or aragonite is increased by addition of L enantiomer, because the transport of growing material is blocked.

To obtain insight into the adlayer formation at an atomic level we performed force-field calculations using the COMPASS force field of the Materials Studio program package.[19] Monocarboxylic acids such as acetic acid, propionic acid, or benzoic acid were found to attach strongly to the $(104) \times (01\bar{4})$ steps of the calcite {104} faces through their carboxylate head groups. A simple test for the binding of carboxylic acids to the surfaces of $CaCO_3$ crystals can be carried out with the aid of the fluorescent dye fluorescein with a carboxylate anchor as an additive during crystallization. Characterization by means of confocal laser scanning microscopy (CLSM) demonstrates the coverage of the crystal surface by the fluorophore (Figure 5).

Amino acids ($RCH(NH_2)COOH$) prefer a bidentate interaction through their amino and carboxylate groups. The binding of the D and L enantiomers differs in the orientation of the residue R at the asymmetric carbon with respect to the surface. To compare the binding motif for both enantiomers, we simulated the chemisorption of a racemic mixture of D- and L-alanine to the $(104) \times (01\bar{4})$ surface step. Figure 6 shows the preferred coordination of L-alanine to the selected surface step as obtained from geometry optimization. Figure 7 shows that the L enantiomer fits better in the chosen surface step.

XPS spectra taken on the (104) surface of freshly cleaved calcite crystals immersed in alanine did not show signals corresponding to an amino acid surface layer, even after long acquisition times. Likewise, thermogravimetric analysis did

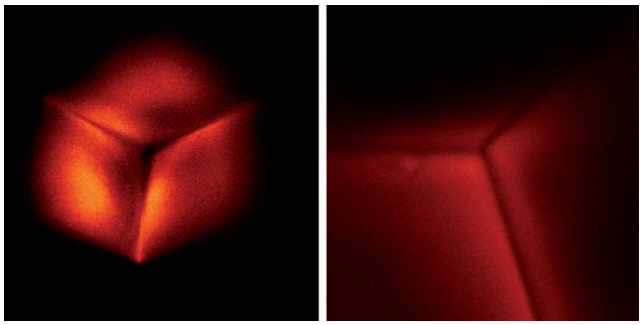

Figure 5. CFLM images of a calcite crystal functionalized with fluorescein.

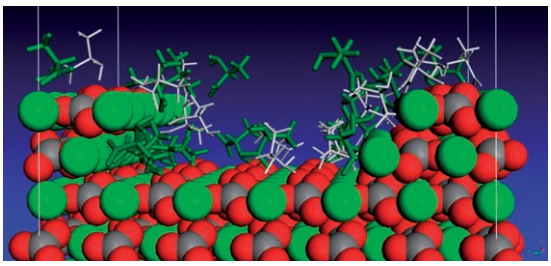

Figure 6. Binding motif of a racemic mixture of alanine computed with the COMPASS force field. The L enantiomer is colored in green and prefers coordination at the left step.

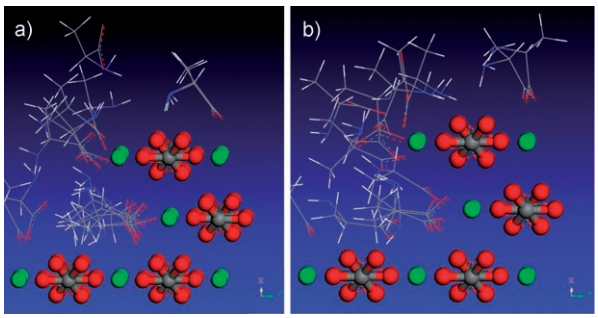

Figure 7. Detailed view of the binding motif from molecular modeling calculation for a) L-alanine and b) D-alanine attached to a (104) step. A higher degree of order is observed in (a) than in (b).

not show any decomposition of organic material. This finding may be explained by amino acid binding to surface step edges and kinks, which is in good agreement with the results of molecular modeling simulations. ^{13}C CP/MAS NMR spectra of carefully washed bulk $CaCO_3$ crystals obtained in the presence of D- and L-alanine, however, revealed weak signals of the amino acid, which may be bound to the outer surfaces of the crystals or occluded in the grain boundaries (see the Supporting Information). Elemental analysis also shows slightly increased nitrogen content for precipitates obtained in the presence of alanine (L: 0.05 %, D: 0.08 %); these values are distinctly lower, however, than for crystallites with pronounced domain structure (composite structure).

The above results support a model in which differences in the surface binding of the amino acid enantiomers have a pronounced influence on the phase selection of $CaCO_3$. In contrast to a 3D crystal, on a 2D surface only mirror planes perpendicular to the surface are allowed (i.e. all symmetry operations for racemic arrangements that activate positions underneath the surface are not available). This is the basis for the *P*1 symmetry of the low-indexed (104) crystal surface of calcite, and most high-indexed (stepped) surfaces also exhibit triclinic symmetry, which allows the formation of diastereomeric aggregates between the surface and chiral adsorbate molecules.

Our results demonstrate that chiral additives selectively inhibit the crystallization of a more stable polymorph by adsorbing to a chiral surface. Nucleation and crystal growth are not only an expression of equilibrium energetics, but also of the growth kinetics, which, in turn, is controlled by surface molecules chemisorbed at kinks on atomic ledges. The selective binding of chiral amino acid additives to the crystal surface sites thus allows growth kinetics to dominate the crystallization process, thereby leading to the formation of a metastable $CaCO_3$ polymorph.

In conclusion, we have demonstrated for the first time that the phase selection of $CaCO_3$ is dependent on the chirality of the additives used in the crystallization. Although chirality is a common feature in nature, previous efforts to elucidate the effects of chiral additives are remarkably scarce and restricted almost exclusively to the control of crystal morphology. This contribution explores for the first time the use of chiral additives in polymorph control of minerals by addressing the issue of chiral adlayers on polymorph selection.

Our results may also point to a possible mechanism for the prebiotic synthesis of homochiral amino acids and polypeptides[20] and may also have implications for asymmetric catalysis.[21] 1) Chirally selective adsorption occurs preferentially on calcite surfaces with terraced growth features. This phenomenon suggests that a local, highly selective concentration of one enantiomer may arise along steplike features, with calcite serving as a possible template during the formation of homochiral amino acids from achiral precursors. 2) Furthermore, the local concentration of only one enantiomer may favor an alignment of homochiral amino acids, which is needed to promote homochiral polymerization[22] and considered to be a key step in the synthesis of self-replicating peptides.[23] Mineral-mediated chiral selectivity, in conjunction with the formation of homochiral polymers, may thus provide a link between prebiotic synthesis and the world of RNA and proteins.

The presented results may also have implications for origin-of-life scenarios. It is presumed that racemic amino acids existed during the Archaean period, either from exogenous sources[24] or from prebiotic synthesis.[25] This study demonstrates that calcite and other minerals may have provided a mechanism for the concentration and chiral selection of these amino acids.[26]

Experimental Section

In all experiments, ultrapure water was used (> 18.2 MΩ, Millipore Synergy 185). Glass slides, used for sample collecting, were cleaned with a solution of ammonia (28–30 %) and hydrogen peroxide (30 %) in water (1:1:5 ratio by volume) at 80 °C for 10 min. The slides were

rinsed with ultrapure water and blown dry with nitrogen (99.999%). Crystallization was carried out by the slow-diffusion technique. Each enantiomer of the amino acids (250 mg, Acros or Sigma-Aldrich, >98%) was diluted in a $CaCl_2$ solution (250 mL, 10 mmol, Merck, Suprapur), in some cases with the help of ultrasonication. Then, the solutions of the L and D form of the same amino acid (typically pH value about 7) were placed in the same desiccator and incubated at 25°C over freshly grounded ammonium carbonate (14 g, Acros, p.a.) in incompletely sealed vessels, containing cleaned glass slide to collect the crystals. The crystallization was carried out at 25°C and stopped after 2 days by removing the slides and washing them with water to remove weakly adhered crystals. After this period, the homogenous precipitates were collected and further investigated. The pH value of the starting solution was not adjusted, because of the well-known effect of foreign ions on the precipitation of calcium carbonate.

The two crystallization vessels were placed in a desiccator with a side tube through which the cables of the electrodes were passed outside to the processing unit. A WTW SenTix 81 pH electrode with automatic temperature compensation, a WTW Ca800 Ca^{2+}-sensitive electrode, and two WTW pH/Ion 340i processing units were used to monitor the progression in intervals of 5 minutes. For alanine, $[Ca^{2+}]$ in the supernatant solution was determined by means of atomic absorption spectroscopy. The L form was found to contain 1.3 $mg\,mL^{-1}$ and the D form 0.8 $mg\,mL^{-1}$.

The scanning electron microscopy (SEM) imaging of the $CaCO_3$ particles was performed on a Zeiss DSM 940 (acceleration voltage 3–15 kV, working distance 5–7 mm). Small sections of the glass slides were fastened with conductive carbon tabs onto aluminum sample holders. For better conductivity, the samples were sputtered with 10 nm of gold (Baltec MED020).

Elemental analysis of the precipitate: Blank test 0.04% N; in the presence of L-alanine 0.05% N; in the presence of D-alanine 0.08% N. CP/MAS NMR investigations were performed on $CaCO_3$ obtained in the presence with L- and D-alanine by acquiring data over 4 days. X-ray diffraction patterns were recorded in transmission mode (Siemens D5000, $Cu_{K\alpha 1}$ radiation, Braun M50 PSD).

Materials Studio v4.0 from Accelrys was used for molecular modeling calculations and dynamic simulation.[19] An initial comparison between the results of ab initio calculations with DFT (PB91, GGA) and the COMPASS[19] force field confirmed that electrostatic interactions dominate and that the computational results are well reproduced by using the less time-consuming calculations with the COMPASS force field. The geometry of the additives L- and D-alanine were optimized with Forcite by using the COMPASS force field and an atom-based summation method. Starting geometries of the bulk calcite crystal were obtained by the cleavage of a (104) surface at a depth of 21.25 Å and the subsequent construction of a 3×4 supercell. The bulk crystal was constrained to fixed Cartesian positions, and a two-layer-deep $(104) \times (01\bar{4})$ calcium-terminated step was used. Calcium-terminated steps were used because the crystallizations were performed with the slow-diffusion technique, and so there is excess calcium in solution. The starting geometries of the additive were produced by the construction of an amorphous cell of 50 molecules for the given size of the bulk crystal. After layering (see the Supporting Information), the geometry was optimized with the Forcite package and the COMPASS force field at ultrafine quality (500000 iterations at maximum). Afterwards, a 10 ps Forcite quench (ultra-fine, COMPASS force field with Ewald summation) was performed, to study the stability of surface-bound amino acids (see the Supporting Information).

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[16] The apparent Ca^{2+} concentration in excess of the nominal Ca^{2+} content (10 mmol) of the parent solution is due to the fact that the Ca^{2+}-sensitive electrode is also sensitive to H^+ and NH_4^+.

[17] Match 1.4c, Crystal Impact, Bonn, **2006**; PDF-2, Release 2004, JCPDS-International Centre for Diffraction Data, Newtown Square, PA 19073-3273, USA.

[18] To check that the complexation of Ca^{2+} through the multidentate amino acid ligand is a determining factor, the chiral α-alanine was replaced by the achiral β-alanine. In contrast to experiments using the achiral glycine, β-alanine resulted in the preferential formation of aragonite needles (see the Supporting Information).

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