# Spontaneous Resolution: From Three-Dimensional Crystals to Two-Dimensional Magic Nanoclusters

**Meir Lahav and Leslie Leiserowitz***

The milestone experiment of Louis Pasteur in 1848 on the manual separation of enantiomorphous crystals of sodium ammonium tartrate tetrahydrate laid the foundations of modern stereochemistry.[1a] This observation has intrigued scientists since it demonstrated for the first time that certain classes of molecules display enantiomerism even in solution. It also paved the way for the inspiring suggestion made two decades later independently by van't Hoff and by LeBel of a tetrahedral arrangement of bonds around the carbon atom.[1b,c]

The experiment by Pasteur comprises two distinct steps. The first involves the spontaneous segregation of the two enantiomers of the racemic mixture into distinct enantiomorphous crystals. The second step involves the manual separation of these enantiomorphs by taking advantage of the hemihedral morphology that these crystals express, as manifested by opposite crystal faces that do not develop to the same extent (Figure 1).

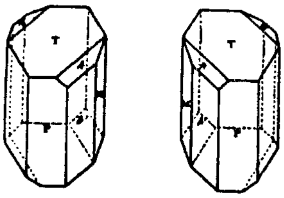
**(a) Dextrorotatory. (b) Lævorotatory.**

Figure 1. Representation of enantiomorphous crystals of sodium ammonium tartrate tetrahydrate (drawing reprinted with permission from G. Kauffman, I. Bernal, H.-W. Schutt, *Enantiomer*, **1999**, *4*(1), 33).

The question as to whether enantiomers aligned on an interface will separate into two-dimensional crystallites of opposite handedness has long been a puzzle. Unlike in three-dimensional crystals, the detection of spontaneous segregation of enantiomers in two dimensions is not straightforward. Only recently, with the advent of modern analytical tools such as scanning probe microscopy (SPM)[2–4] or grazing incidence X-ray diffraction (GIXD),[5–7] has it become possible to demonstrate unambiguously the spontaneous segregation of enantiomers in enantiomorphous two-dimensional crystallites on solid or liquid surfaces.

Recently the groups of R. Berndt from Aachen and W.-D. Schneider from Lausanne reported a two-dimensional analogue of the Pasteur experiment. Deposition of 1-nitronaphthalene from the vapor phase on gold surface yielded clusters that are one layer thick. The most common (85%) among these were decamers that displayed chiral shapes of opposite handedness (i.e., enantiomorphism) in two dimensions. Furthermore, no less remarkable, these small clusters could be physically moved on the gold surface without being destroyed, and subsequently separated into enantiomorphs (Figure 2a, b).[8, 9]

Although 150 years have elapsed since the Pasteur experiment, various aspects of this process are still of interest. For example, despite the considerable body of data that has been collected on crystal structures, our present knowledge of intermolecular interactions does not suffice to predict which racemates will crystallize as conglomerates or form a racemic crystal. The problem belongs to the general one of predicting crystal structures, where the central question to be addressed is how molecules are arranged to build periodic arrays. An ab initio prediction of possible molecular packing modes leading eventually to the observed crystal structures remains fraught with difficulties, although tremendous progress has been made in the development of computational methods.[10] A major deficiency lies in the determination of precise atom–atom potential parameters that dictate the conformation and packing of molecules in crystals.

The second aspect concerns the absence or presence of hemihedral faces in chiral crystals, and how observed hemihedrism may be correlated with the molecular chirality, which is part and parcel of the problem of predicting crystal morphology. The question of whether a chiral crystal develops hemihedral faces is a consequence of the difference in interactions between the surfaces of opposite crystal faces $(h,k,l)$ and $(-h,-k,-l)$ and their environment. The theoretical growth form of a crystal, corresponding to growth under vacuum, may be determined from the computed inter- and intralayer energies of the crystal following the basic rules for a quantitative determination of crystal morphology laid down by Hartman and Perdok.[11] However, a solution-grown crystal

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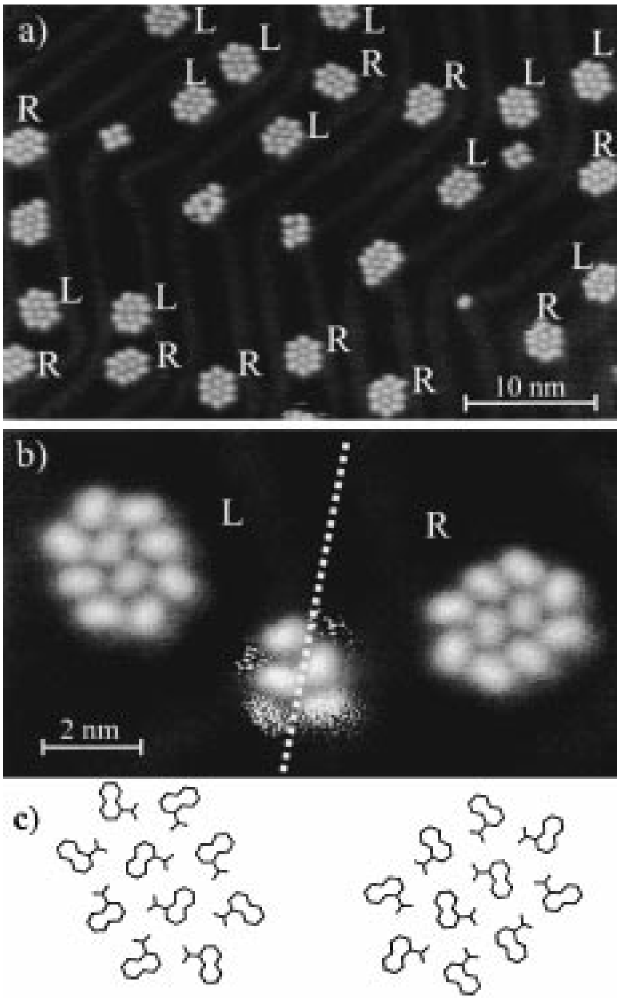

Figure 2. a) Two-dimensional chiral clusters (L and R) formed by 1-nitronaphthalene molecules on the Au(111) surface. About 85% of the molecular aggregates are decamers. b) Pasteur-type experiment involving manual separation of the (L)- and (R)-decamers on the gold surface. c) The molecular arrangement within the decamer as determined by molecular dynamics simulations.

requires a computation of the interactions between the solvent and the different faces of the crystal. Crystal hemihedrism can be induced by modification of the morphology of one of the enantiomorphs by the addition of tailor-made additives that interact enantioselectively with the faces of the enantiomorph to be affected.[12]

The detection of spontaneous separation of enantiomers from a racemic mixture in two dimensions at an interface awaited the development of modern surface analytical tools, as alluded to above. Chiral discrimination of molecules in solution and in two-dimensional Langmuir films has been examined theoretically by Andelmann and de Gennes,[13] by considering interactions only within a molecular pair. Their overall conclusion that heterochiral pairs should be generally favored is relevant to dilute fluid phases, but hardly to crystalline systems, where multiple molecular interactions and crystal symmetry play a dominant role.

On symmetry grounds spontaneous separation of enantiomers in two dimensions at an interface should be a more simple process than in three dimensions, particularly for amphiphilic molecules aligned on the water surface. For such monolayer systems, the center of inversion, the glide whose plane is parallel to the surface, and the twofold screw axis parallel to the water surface are precluded. A twofold symmetry axis perpendicular to the plane of the interface may also be excluded since it generally does not lead to close molecular packing. Therefore the only remaining crystallographic symmetry elements that may appear in plane groups are translation and the glide whose plane is perpendicular to that of the interface. To induce separation of chiral territories, the glide symmetry and possible formation of a solid solution between the two enantiomers have to be prevented.

We need not dwell upon the three-dimensional crystallization of nonchiral molecules in chiral space groups, the process being not uncommon. The interaction of nonchiral molecules with planar surfaces leads to a reduction in symmetry and thus to a limitation of the symmetry elements required for generating a two-dimensional array, as already alluded to above for amphiphilic molecules in contact with the water surface. Furthermore, we may expect that the surface-bound nonchiral molecule will assume a chiral conformation, as was found for nitronaphthalene on gold.

Several examples of spontaneous segregation of racemic mixtures into two-dimensional crystals on planar surfaces by applying SPM methods have already been reported. Eckart et al. observed segregation on a mica surface by SPM.[3] Walba et al. described the separation of enantiomers on a graphite surface,[2] and de Schryver, Müllen et al. reported the organization of nonchiral amphiphilic molecules into chiral domains as detected by scanning tunneling microscopy (STM).[4]

Weis and McConnell had observed, by epifluorescence measurements, the existence of chiral patterns of monolayers of amphiphilic molecules of a single handedness on aqueous solutions.[14] By applying the same method, Rietz et al. reported an example where racemic diols assume chiral patterns on the surface of water.[15] However, grazing incidence X-ray diffraction (GIXD) measurements on the same system yielded two-dimensional crystals composed of a rectangular unit cell, in agreement with the formation of a true racemate. Selinger and Selinger pointed out that the formation of spiral defects in two-dimensional aggregates lead to chiral symmetry breaking on the macroscopic length scale, even without any microscopic chiral order.[16]

Lundquist proposed, from a comparative study of molecular area surface pressure isotherms of Langmuir monolayer films of enantiomeric and racemic amphiphiles, that certain racemates undergo spontaneous resolution.[17] Following this approach, Arnett and Stewart suggested that racemic mixtures of myrisothylalanine ($C_{17}H_{35}CONH(CHCH_3)COOH$) separate into islands of opposite handedness.[18] This separation into chiral territories was unambiguously established by Rondelez et al. using GIXD.[5] As part of studies on the origin of optical activity on Earth, we have used the method of GIXD to demonstrate that racemic mixtures of several $\alpha$-amino acids, such as palmitoyllysine, spontaneously separate into chiral two-dimensional islands, whereas other $\alpha$-amino acid mixtures form racemic compounds.[6] This behavior is illustrated in Figure 3, which shows the GIXD patterns of monolayer crystallites of racemic and optically resolved amino acids at the air–solution interface. A detailed analysis of the GIXD data by X-ray structure factor computations revealed the molecular structures to near atomic resolution. A GIXD pattern of a racemic monolayer system may imply a general separation of chiral territories, but in itself cannot preclude the presence of partial mutual solubility of the two enantiomers, as was recently demonstrated by a GIXD study of mixtures of long chain substituted mandelic acid and phenylethylamine.[7]

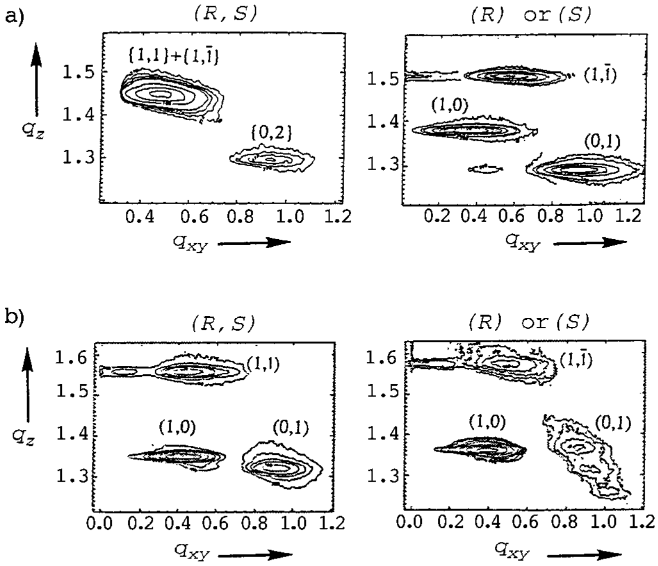

Figure 3. The GIXD patterns of $\alpha$-amino acid amphiphiles on water as a function of the horizontal ($q_{xy}$) and vertical components ($q_z$) of the X-ray scattering vector $q$ (given in units of Å$^{-1}$). a) The GIXD patterns of the racemic, ($R$,$S$), and enantiomeric, ($R$) or ($S$), monolayer clusters of $C_{16}H_{33}CH(NH_3^+)COO^-$ are different, in keeping with the two-dimensional crystallization of a racemic compound of the $R$,$S$ mixture whose $R$ and $S$ molecules are related by glide symmetry. b) The GIXD patterns of the racemic, ($R$,$S$), and enantiomeric, ($R$) or ($S$), monolayers of $C_{17}H_{35}CONHC_4H_8CH(NH_3^+)COO^-$ are similar, in keeping with a separation of $R$ and $S$ molecules into two-dimensional crystals of opposite handedness.

In all these studies on solid and liquid surfaces, the element of manual separation of the chiral crystallites of opposite handedness was missing. In the experiments by the groups of Berndt and Schneider, which involved the self-segregation of nitronaphthalene in the form of two-dimensional chiral clusters followed by a physical sorting of the left- and right-handed clusters, this part of the Pasteur-type experiment was completed. What is remarkable in this experiment is that these magic clusters are composed of ten molecules only. The arrangement of the ten molecules within these clusters (Figure 2c), determined by molecular dynamics computations, shows no true periodicity. The eight molecules exposed on the periphery of the cluster are of the same chirality, whereas the remaining two molecules within the cluster are of opposite chirality. The molecules reside flat on the gold surface, and the interactions between the clusters and the gold surface are weak. The molecules within the clusters are held together primarily by weak C–H ⋯ O interactions, and yet the clusters are sufficiently stable to be moved on the gold surface without perturbing their integrity. This manipulation is accomplished by positioning the tip on top of the cluster to be moved. At that position the tunneling resistance is decreased by three orders of magnitude.

One century after the discovery by Pasteur, stereochemistry was placed on an absolute basis by Bijvoet et al.,[19] who applied the method of anomalous X-ray scattering to enantiomorphous crystals for the assignment of the absolute configuration of the constituent chiral molecules. This method became readily applicable to structures containing heavy atoms; for molecules containing light atoms only such as C, N, or O the method is fraught with experimental uncertainties when applied in a conventional way. This barrier may be circumvented by inducing a change in the morphology of chiral or centrosymmetric crystals when grown or dissolved in the presence of tailor-made chiral auxiliaries, leading to a direct assignment of the sense of chirality of the auxiliary molecules and the chiral crystals.[12]

The imaging of the morphology of chiral molecular clusters to near atomic resolution, coupled with modern computational methods, provides an additional independent analytical tool for the direct assignment of absolute sense of molecular chirality.

Finally, the results described on nitronaphthalene suggest that the self-organization of nonchiral molecules into two-dimensional chiral clusters at interfaces might prove to be a frequent process. Such types of clusters could serve as matrices for absolute asymmetric transformations, akin to these reported in three-dimensional crystals. Such chemical reactions might have played a ubiquitous role in the transformation from racemic chemistry to chiral biology in prebiotic days.

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**Keywords:** enantiomeric resolution · monolayers · nanostructures · scanning tunneling microscopy · X-ray diffraction

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# Homopolyatomic Nitrogen Compounds**

## Thomas M. Klapötke*

As a consequence of the high thermodynamic stability of the $N_2$ molecule other homopolyatomic nitrogen species are very rare. Dinitrogen, $N_2$, was first isolated in 1772 by D. Rutherford and also by C. W. Scheele and H. Cavendish (Figure 1).[1] Over 100 years later hydrazoic acid, $HN_3$, was prepared for the first time by T. Curtius, and numerous metal azides containing the linear, isolated $[N_3]^-$ ion have been characterized (Figure 1).[2] Sodium azide can be prepared by adding powdered $NaNO_3$ to fused $NaNH_2$ at 175 °C or by passing $N_2O$ into the same molten amide at 190 °C [Eqs. (1) and (2), respectively].[1]

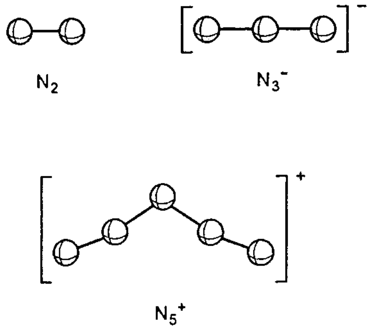

Figure 1. Structures of the isolated homopolyatomic polynitrogen species $N_2$, $N_3^-$, and $N_5^+$.

$$NaNO_3 + 3\,NaNH_2 \xrightarrow{175\,^{\circ}C} NaN_3 + 3\,NaOH + NH_3 \tag{1}$$

$$N_2O + 2\,NaNH_2 \xrightarrow{190\,^{\circ}C} NaN_3 + NaOH + NH_3 \tag{2}$$

In covalently bound azides the $N_3$ group behaves as a pseudohalogen (for example in $HN_3$ and the halogen azides $FN_3$, $ClN_3$, $BrN_3$, and $IN_3$),[3] and although potential allotropes of nitrogen such as $N_3$–$N_3$ (analogous to $Cl_2$) and $N(N_3)_3$ (analogous to $NCl_3$) have not been unequivocally isolated the compounds have been extensively studied by quantum chemical methods (see below). The predicted high instability of any potential homopolyatomic nitrogen species stems from the particularly strong N–N triple bond in $N_2$ that has a bond energy of 226 kcal mol$^{-1}$, which is much higher than three single bonds ($3 \times 37.8$ kcal mol$^{-1}$), a single and a double bond ($37.8 + 99.9$ kcal mol$^{-1}$) or 1.5 times the average N–N double bond energy ($1.5 \times 99.9$ kcal mol$^{-1}$).[4]

Quite recently K. Christe and co-workers reported on the fundamentally and surprisingly straightforward preparation and characterization of the salt $[N_5]^+[AsF_6]^-$ in anhydrous HF [Eq. (3)]. This salt contains the novel $N_5^+$ cation (Figure 1),

$$N_2F^+[AsF_6]^- + HN_3 \xrightarrow{HF,\ -78\,^{\circ}C} N_5^+[AsF_6]^- + HF \tag{3}$$

which represents only the third stable member of the $N_n$ family made in this century.[5] Certainly, Karl Christe and co-workers deserve warm congratulations on this! The synthesis of this $N_5^+$ species is therefore a major breakthrough in research centered on the investigation of the elusive $N_n$ species. The interest in the formation of the $N_5^+$ cation is not only that it is such a novel compound, but also for its potential to act as a precursor to many more polynitrogen systems. The new compound $[N_5]^+[AsF_6]^-$ is a white solid with marginal stability at room temperature but which can be stored for weeks at −78 °C.

The existence of the $N_5^+$ cation was first predicted by P. Pyykkö and N. Runeberg.[6] However, these authors found a $^3\sigma$ ground state $[(N{\equiv}N)\cdots(N_3)]^+$ for $N_5^+$. The symmetrical $C_{2v}$ $^1\sigma$ state of $N_5^+$, which has now been observed experimentally by Christe et al., lies 1.962 eV above the asymmetrical triplet at the MP2 level of theory. However, Pyykkö and Runeberg had already pointed out that the very different geometry of

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