

Supramolecular Chemistry

One-Dimensionally Disordered Chiral Sorting by Racemic Tiling in a Surface-Confined Supramolecular Assembly of Achiral Tectons

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Abstract: The aggregation of (pro)chiral/achiral molecules into crystalline structures at interfaces forms conglomerates, racemates, and solid solutions, comparable to known bulk phases. Scanning tunneling microscopy and Monte Carlo simulations were employed to uncover a distinct racemic phase, expressing 1D disordered chiral sorting through random tiling in surface-confined supramolecularly assembled achiral 4,4"diethynyl-1,1':4',1"-terphenyl molecules. The configurational entropy of the 1D disordered racemic tiling phase was verified by analytical modeling, and found to lie between that of a perfectly ordered 2D racemate and a racemic solid solution.

Crystallization in racemic solutions usually results in conglomerate or racemic compounds, or solid solutions.^[1] The invention of scanning tunneling microscope (STM)^[2] provided access to submolecular resolution of (pro)chiral patterns, enabling fundamental insights into conglomerate and racemic crystallization mechanisms and processes at interfaces.^[3] In the case of 2D conglomerate crystals, homochiral molecular ensembles or bonding motifs usually form periodic superlattices in enantiopure domains (Figure 1 a),^[4] while for 2D racemic crystals, heterochiral molecular ensembles or bonding motifs are arranged either in an alternating manner^[5] or following line-wise stacking^[6] (Figure 1b). A third, rarely observed possibility is 2D random solid solution,^[7] in which the distribution of enantiomers on a periodic lattice is random (Figure 1d). At the same time, however, the molecular adsorption footprints may obey strict heterochiral arrangement conventions.^[7a]

The definition of a crystal based on translational symmetry in real space was widened upon the discovery of quasicrystals.^[8] Nowadays the notion of crystallinity is defined

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Figure 1. Illustration of the 2D solid phases from chiral elements. a) Regular conglomerates. b) Regular racemates. c) A distinct racemate with 1D randomness in chiral sorting. d) Random solid solution. *R* and *S* denote the respective handedness of the chiral molecule or bonding motif. For simplicity, a 2D square lattice is assumed for all crystals.

by the International Union of Crystallography (IUCr) as, "...any solid having an essentially discrete diffraction pattern".^[9] Accordingly, the current understanding of crystals also includes condensed matter systems without perfect lattice periodicity, which incorporate structural disorder or randomness. Within the field of 2D crystallization, research focusing on periodic^[10] and non-periodic surface tilings^[11] has received considerable attention. Intriguingly, the rhombus random tiling in a 2D molecular system was discovered^[12] and identified as an equilibrium state^[13] reflecting maximum entropy in the system. Another fundamental question arising from thermodynamically stable random tiling is its implication in chiral self-sorting.^[1]

Herein, we identify a distinct racemic phase with 1D randomness in chiral sorting (Figure 1 c), featuring an intrinsic degree of disorder with entropic origin. More specifically, we investigate the self-assembly of 4,4"-diethynyl-1,1':4',1"-terphenyl (DETP) on the smooth Ag(111) surface by STM assisted with Monte Carlo (MC) simulations. DETP monomers with equivalent adsorption registry express porous domains through $C-H\cdots\pi$ interactions among terminal



alkynes. The bonding motif features a threefold symmetric, chiral node, existing in two enantiomorphs. Porous networks of varying sizes are observed, which contain several types of well-defined pore shapes representing tiles; these can be classified with respect to their enantiomorphous excess of chiral nodes into homochiral, heterochiral, and a distinct racemic phase with 1D randomness. Although all three types of networks can be realized in principle, we found that larger domains are solely expressed as the racemic type. The experimental findings are complemented by MC simulations. To classify this phase in relation to solid states from chiral compounds, we employ a tiling representation and calculate the configurational entropy for each network type. We show that the 1D disordered random tiling can be categorized as a distinct racemic phase between 2D regular racemates and random solid solutions (Figure 1). Although local crystallographic defects (that is, vacancies and Y-shaped bonding motifs) are identified, we will show that they can be excluded as the source of the disorder in the networks.

The chemical structure of DETP is shown in the inset of Figure 2a. The backbone of the molecule consists of three phenyl rings and is functionalized with terminal alkyne groups at opposite ends. This linear tecton exhibits $C_{2\nu}$ symmetry and has no point chirality.^[3b,e] A sub-monolayer coverage sample was prepared by depositing a small amount of DETP molecules onto the Ag(111) substrate held at $T_{sub} = 200$ K and subsequently cooled to T < 10 K. The STM data depicted



Figure 2. a) STM image of a low-coverage sample ($U_b = -1.0$ V, $I_t = 0.1$ nA) measured at 4.5 K. The close-packed substrate directions are indicated at the lower left with a white star. Different types of small domains are denoted: molecular clusters (white arrows), single closed pores (blue arrows), and small islands (green arrows). Inset: chemical structure of the DETP unit. b) High-resolution STM images super-imposed with scaled models and registry. The handedness of chiral motifs is color coded, and denoted as *R* and *S*.

in Figure 2a reveals molecular clusters, single closed pores, and small islands distributed over the surface. For all formations, it is found that the long molecular axis of the DETPs follows the $< 11\overline{2} >$ directions (Figures 2 a,b), indicating a preferred epitaxy. Aggregation is mediated by terminal alkyne groups forming a threefold node with neighboring units enclosing a 120° angle (Figure 2b). This bonding motif is very similar to the one observed previously for a threefold symmetric compound with terminal alkynes,^[14] indicating by analogy that the weak C–H··· π bonding^[15] is responsible for the molecule-molecule interaction. The threefold bonding motif exhibits organizational chirality^[3b-f] whereby the handedness of the node is color coded and marked in red and blue for the (R) and (S) isomorphs, respectively. Both enantiomorphs are expressed in two equivalent configurations (Figure 2b) on the sixfold symmetric Ag(111) surface. Importantly, the superposition of the scaled molecular model (see Methods section in Supporting Information) on the STM data suggests a uniform epitaxy of all molecules involved in the bonding motif (Figure 2b). Specifically, the central phenyl ring sits on a bridge site, two outer phenyl rings reside above hollow sites and terminal alkynes on top sites; in good agreement with the expectation for the energy optimized adsorption configuration following the tendencies reported earlier.[14]

Based on the detailed analysis of high-resolution STM data, ten distinct geometries were identified as suitable for the construction of a pore with a continuously connected rim (Figures 3; Supporting Information, Figure S2). These configurations can be classified into three sets by their enantiomorphous excess (ε ; $\varepsilon = (N_R - N_S)/(N_R + N_S)$, where N_i is the number of the nodes of isomorph *i*). For α type (Figure 3a), in which all nodes surrounding one pore express the same handedness, the absolute value of ε equals 1. For β type, $|\varepsilon| =$ 1/3; that is, four of six nodes have the same handedness. Three equivalent geometries are possible because of the symmetry of the substrate (Figures 3b-d). For γ type, the nodes represent a racemic mixture and accordingly $\varepsilon = 0$ (Figure 3e). As for the individual nodes, a consistent epitaxy follows from the modeling of the pores (Supporting Information, Figure S2). By connecting the centers of the six nodes of each pore structure with straight lines, the molecular models can be converted to a tile representation (Figure 3; Supporting Information, Figure S2). Each vertex of the tiles is coded with R or S containing the properties of the chiral nodes. The edge length of SS (or RR) and SR (or RS) is 7a (a = 2.889 Å)and $4\sqrt{3a}$, respectively, and therefore, they are not equivalent.

Firstly, we examine the characteristics of different domain types observed for samples with low coverages (Figure 4). By superimposing molecular models onto high-resolution STM images of various domains, it is found that any molecule in a given network obeys the same adsorption registry as suggested for the nodes and pores (Supporting Information, Figure S3). Figure 4a shows a selected small island with a periodical structure containing exclusively α_R tiles (Figures 4a,b) which is rarely observed (Figures 6a; Supporting Information, Figure S4a). We classify this domain as the homochiral type, since it is formed solely with α tiles and

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Figure 3. All possible configurations for the nanopores. a) Pores with exclusive *S* or *R* nodes (α). b)–d) Pores with either the *R* or *S* node dominating (β). e) Pores with equal numbers of *S* and *R* nodes (γ). Although the γ pore is achiral, it is still denoted by *R* and *S* for consistency. Each pore shape is transformed into a tile when the nodes of the hexagonal pores are linked. The vertex of the tile is encoded with the node chirality of the corresponding pore structure.

accordingly the $|\varepsilon|$ of this domain equals 1. Figure 4c displays another type of domain, which mainly contains α_s and β_s tiles with a $|\varepsilon|$ of approximately 0.45 (Figure 4 d). We refer to such domains with mixed tiles and $0 < |\varepsilon| < 1$ as the unbalanced heterochiral type (termed in the whole paper as heterochiral for simplicity). At a first glance (Figure 4c), this domain lacks periodicity and regularity. However, it can be shown that this domain is an early stage of a long-range ordered complex superstructure with a large unit cell (Supporting Information, Figure S5b-vi). A third type of domain is shown in Figure 4e and its structural analysis unveils contributions mainly from β_{S1} , β_{R3} , and γ_s tiles (Figure 4 f). The balanced number of R and S nodes leads to a negligibly small ε ($|\varepsilon| = 0.06 \approx 0$) for the whole domain; therefore, this type of network is classified as the racemic type. Note, that for all three types of domains the tiling obeys a rigorous rule; that is, the joint vertices must be of the same handedness. The formation of three network types can be rationalized by a stepwise tiling process (see Supporting Information). Accordingly, three essential consequences of the tiling processes are inferred: 1) homochiral and heterochiral networks must follow 2D periodic lattices; 2) the network types are already determined during the initial growth steps and the islands preserve the seed characteristics; 3) homochiral, heterochiral, and racemic tilings are incompatible with each other and therefore cannot intermix without creating crystallographic defects, which are the vacancies (Supporting Information, Figure S7) and Y-shaped bonding



Figure 4. a) STM image and b) tiling of a homochiral domain. c) STM image and d) tiling of a heterochiral domain. e) STM image and f) tiling of a new state reported herein, which features racemic domains with 1D randomness. The close-packed directions of the substrate for each STM image are shown and the ε values of each domain are given. The STM images were selected to highlight different domain types. White dashed lines in (f) are visual guides.

motifs (Supporting Information, Figures S8–S10) observed in the experiments.

For samples prepared with higher molecular coverage, extended networks are formed with continuity up to 200 nm (Supporting Information, Figure S11). Figure 5 a shows a representative STM image of a fully reticulated network. Employing the tiling representation (Figure 5b), the network characteristics can be easily understood. The large domain contains only β_{S1} , β_{R3} , and γ motifs, whereby the arrangement of tiles has 1D translational symmetry along the $[0\overline{1}1]$ direction. However, along the $[\bar{1}10]$ direction, the tiling shows a clear 1D randomness. Interestingly, the β_{S1} and β_{R3} columns are often next to each other or intermittently separated by γ columns (yellow γ_R tiles in Figure 5b; Supporting Information, Figure S11). The space between $\beta_{S1} + \beta_{R3}$ pairs is filled with γ_S tiles (brown). Figure 5c depicts a close-up image of a region (white parallelogram in Figure 5b), where the handedness of the nodes is displayed.

Equivalent to the tiling representation, the handedness of all the nodes in the network naturally bears the 1D randomness along the [$\overline{1}10$] direction and is conserved along [$0\overline{1}1$]. Starting with the front edge of the tiles (along [$\overline{1}10$]), the *R* and *S* nodes always appear as pairs (indicated by dashed lines in Figure 5 c) in the sequence, which naturally results in $\varepsilon = 0$ for the whole domain. We define the [$0\overline{1}1$] direction as the main axis of the domain. Racemic domains with other main-



Figure 5. a) STM data for an extended racemic network ($U_b = -1.0$ V, $I_t = 0.03$ nA). Inset: FFT of a large domain where (a) is embedded; sixfold-symmetric first-order reciprocal spots (red circles); blue arrows point out faint streaks. b) Tiling representation of (a). c) The handedness of the nodes in the selected part of the network. The black dashed lines in (c) are visual guides, which distinguish *RS* or *SR* pairs and correspond to the white dashed lines in Figure 4 f. The discontinuity markers, as well as the ellipsis in (c), indicate the omission of identical rows for simplicity.

axis directions were similarly observed (Supporting Information, Figure S12). The respective 2D fast Fourier transform (2D FFT) into reciprocal space yields sharp and discrete spots along with a weak diffuse pattern, thus classifying the tiling pattern as crystalline according to the definition of the IUCr. Intriguingly, the sharp reciprocal spots correspond to an ideal 2D periodic network containing only γ tiles (Supporting Information, Figure S11c). The reasons for this are simple: along $[0\overline{1}1]$ (the main axis), the tiling has 1D translational symmetry with an invariable distance of 12a (a = 2.889 Å) between neighboring tiles; along $[\bar{1}10]$, despite the disorder the averaged length of $\beta_{S1} + \beta_{R3}$ pairs amounts to 12*a* as well (Supporting Information, Figure S13). The faint streaks (blue arrows in Figure 5a) cutting through the reciprocal spots along a direction perpendicular to $[0\bar{1}1]$ (in real space) reflect the 1D disorder along $[\bar{1}10]$. Hence, we define the 2D racemates as a 2D quasi-periodic crystalline network.^[9] For further confirmation of the correlation between the pattern in reciprocal space and the network ordering, we constructed an ideal, artificial racemic network following the tiling rules (Supporting Information, Figure S14) and found that its 2D FFT nicely reproduces the two essential features of the experimental case.

Surprisingly, a statistical analysis revealed that, although all three types of networks coexist for small domains (Figure 6a), the tendency towards negligible ε indicates that 2D racemates become the prevailing type with increasing domain size. To understand this phenomenon, we first carried out MC simulations. The calculations were performed with four different coverages, corresponding to a total molecular number (N) of 50, 100, 150, and 200 (Figures 6c,d); the domain-size dependent $|\varepsilon|$ is depicted in Figure 6d. For small N (50 and 100), the $|\varepsilon|$ of the resulting structures are distributed from 0 to 1, indicating the presence of all three forms of porous domains. Upon increase of N to 150, no sample is found exhibiting $|\varepsilon|=1$, showing the absence of



Figure 6. a) The experimental statistics for $|\varepsilon|$ versus *N* (number of molecules in an isolated network) obtained from a large number of networks. b) -TS versus *N* obtained from analytical models of three types of networks, as well as an ideal racemic solid solution. c) Selected MC-simulated structures formed at different *N* values. d) Statistics for MC-simulated $|\varepsilon|$ versus *N*.

homochiral domains. At the highest N (N=200), the $|\varepsilon|$ of the samples stays below 0.3, revealing that racemic domains prevail. The MC simulated $|\varepsilon|$ versus N agrees nicely with that observed in experiments (Figure 6a).

As developed and explained earlier,^[16] it follows from the third law of thermodynamics that the configurational entropy of all static perfect crystals is zero irrespective of the complexity of their unit cells. However, as already pointed out by Pauling,^[17] crystalline forms of ice contain residual configurational entropy, as randomness at the molecular level gives rise to an ensemble of energetically degenerate configurations (W). From the above analysis, we know that the 1D randomness in the racemic networks allows a large number of W of accessible tilings; that is, the different R or S arrangements on a lattice, with the same system energy (see Supporting Information). Accordingly, we calculate W as a function of domain size of an ideal rhombic network containing $M \times M$ tiles for homochiral, heterochiral, and racemic tilings, as well as an idealized 2D racemic solid solution using derived analytical expressions (see Supporting Information) [Eqs. (1)–(5)]:

$$-TS = -Tk_{\rm B}lnW \tag{1}$$

Homochiral :
$$W = 3 \times 2$$
 (2)

Heterochiral:
$$W = 3 \times 2 \times \left(\sum_{j=2}^{M} j^2 + \sum_{k=M+1}^{2M-1} \sum_{l=1}^{2M-k} 2l \right)$$
 (3)

Racemic:
$$W = 3 \times (2^{M+2} + 2^{2M} - 2^2)$$
 (4)

Racemic solid solutions :
$$W' = 3 \times \frac{N'!}{[(\frac{N'}{2})!]^2}$$
 (5)

Here $k_{\rm B}$ is the Boltzmann constant and N' is the total number of chiral nodes of the solid solution. The factor 3, appearing for all types, originates from the possible registries

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with respect to the substrate. Note that for the racemic type, the 1D disordered tilings prevail compared with the 2D periodic tilings (Supporting Information, Figure S15 c). We chose T = 100 K, where reversible bonding association and dissociation is operative (Supporting Information, Figures S16 and S17).

As depicted in Figure 6b, with increasing N, TS of racemic networks increases faster than that of homochiral and heterochiral networks; although it is slower than that of a racemic solid solution, which cannot be realized because of the tiling rule. Hence, the predominant formation of large racemic networks is ascribed to entropic contributions. For a domain at a given amount of molecules (N), although the enthalpy H (intermolecular and molecule–substrate interactions) is equivalent for three types of networks, the configurational entropy promotes the selection of seeds belonging to the 1D disordered racemic type at the initial growth stage. Once a critical seed size is accomplished, the system keeps the seed type during further growth, according to tiling rules.

Notably, a strain–relaxation induced conglomerate– racemate transition was previously observed in the (M)- and (P)-heptahelicenes on Ag(001).^[6d] Such strain-related mechanisms can be excluded in our case as homochiral, heterochiral, and racemic structures are simultaneously observed for small domains (Figure 4, Figure 6a; Supporting Information, Figure S4), and the molecule–molecule and molecule–substrate interactions therein are identical. Finally, the 1D disorder in the racemic network is intrinsically different from the crystallographic defects as the 1D randomness results from the flexibility in the tiling sequence without altering the binding energy, in marked contrast to vacancies or Y-shaped defects.

In conclusion, we introduced 1D disordered racemic tiling as a distinct phase, which is intermediately positioned between a perfectly ordered racemate and a random solid solution with respect to the randomness in chiral-sorting embedded in the crystalline structure. These findings reveal a novel ordering phenomenon related to Pauling's configurational entropy. Our results provide exquisite insights into crystallization and chiral sorting at the molecular level.

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Conflict of interest

The authors declare no conflict of interest.

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