# Supporting Information for "Random and ordered phases of off-lattice rhombus tiles"

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## METHODS

We used a collection of Monte Carlo algorithms to study tiling thermodynamics and dynamics. Simulation boxes were rhombus-shaped and periodically replicated in imitation of bulk surroundings. To study the packing of hard rhombi (Fig. 1, main text) we used standard constant-pressure moves [1], single-particle Metropolis translations and rotations [1], and the following 3-particle rotation algorithm. Starting from microstate 1 (say), we selected at random a tile $i$, and then selected at random any two tiles able to interact with it through the specific interaction (even though $\epsilon_{\rm s} = 0$). We call such particles 'H-bonded neighbors'. If fewer than two such neighbors existed, the move was aborted. Otherwise, we rotated our three chosen particles by 60° (with either sense) about their center of mass, defining a proposed new microstate 2. We accepted this rotation with probability $\min(1, n_1(n_1-1)/[n_2(n_2-1)]\exp(-\beta\Delta E))$. The variable $n_1$ is the number of H-bonded neighbors possessed by tile $i$ in microstate 1; the factor it appears in accounts for the fact that tile $i$ might have a different number of H-bonded neighbors following the proposed rotation. The term $\Delta E$ is the change of energy following the move. This algorithm, effectively a rigid rotation of trimers arranged in compact near-hexagon arrangement, allows efficient conversion between ordered and random dense tilings.

To study the self-assembly of clusters of interacting rhombi (Fig. 2,3, main text, and Fig. S3) we used standard umbrella sampling of the size of a growing cluster [1, 2] in conjunction with single-particle moves, the virtual-move algorithm [3] of Ref. [4] (to allow collective rearrangements of tilings), the 3-particle rotation algorithm, and grand canonical insertions and deletions of rhombi at constant chemical potential [1]. In Fig. 2, main text, eight independent simulations were done for each rhombus aspect ratio shown. The interconversion of dense tilings (Fig. 4a, main text) was studied using the three-particle rotation algorithm, and dynamic simulations of rhombus self-assembly (Fig. 4b, main text) were done using grand-canonical moves and the virtual-move algorithm.

We characterized solid order using the parameter $\Psi \equiv (0.608n_{\parallel} - 0.392n_{\bar{\parallel}})/(0.608n_{\parallel} + 0.392n_{\bar{\parallel}})$. Here $n_{\parallel}$ is the total number (within the simulation box or the largest cluster, as appropriate) of H-bonds between particles whose long diagonals lie closer to being parallel than nonparallel. $n_{\bar{\parallel}}$ is the total number of all other H-bonds. This order parameter allows us to distinguish random tiled structures ($|\Psi| \approx 0$) from crystalline structures with parallel order ($\Psi \lesssim 1$) or nonparallel order ($\Psi \gtrsim -1$; see Fig. S1 for examples of these phases).

We also carried out density functional theory (DFT) calculations [5] of TPTC in vacuum (Figs. 1 and 3, main text) using the B3LYP [6] functional and the the 6-311+G$^\star$ basis set. This basis set includes both diffuse and polarization functions.

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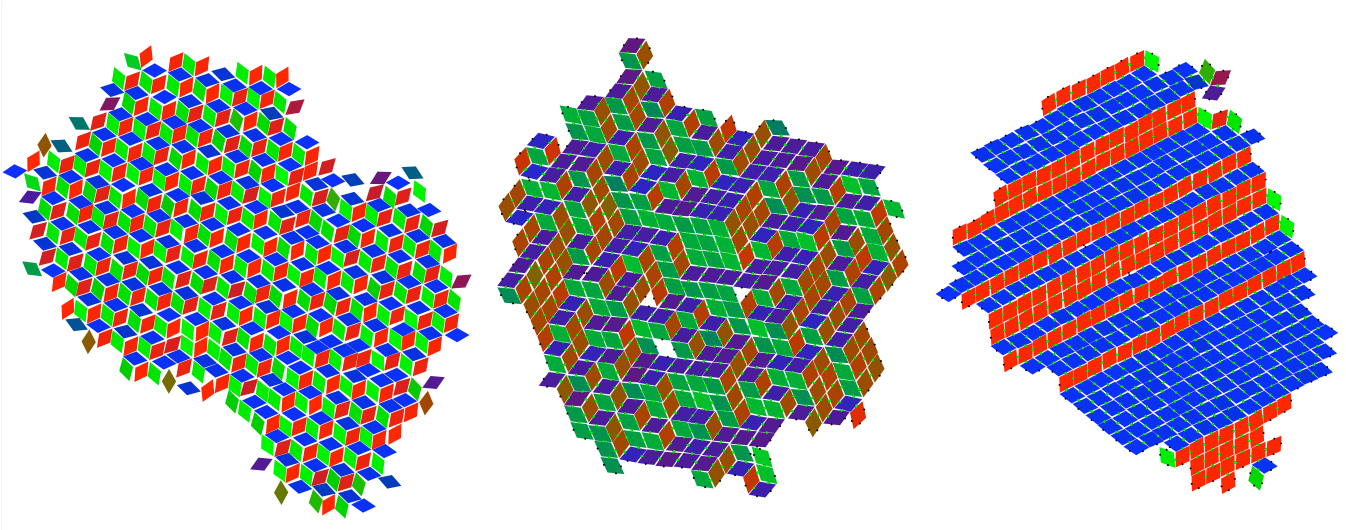

FIG. S1: Snapshots of nonparallel ordered ($\Psi \approx -0.7$)-, random ($\Psi \approx 0$)- and parallel ordered ($\Psi \approx 0.5$) tilings, from left to right. See introduction, main text.

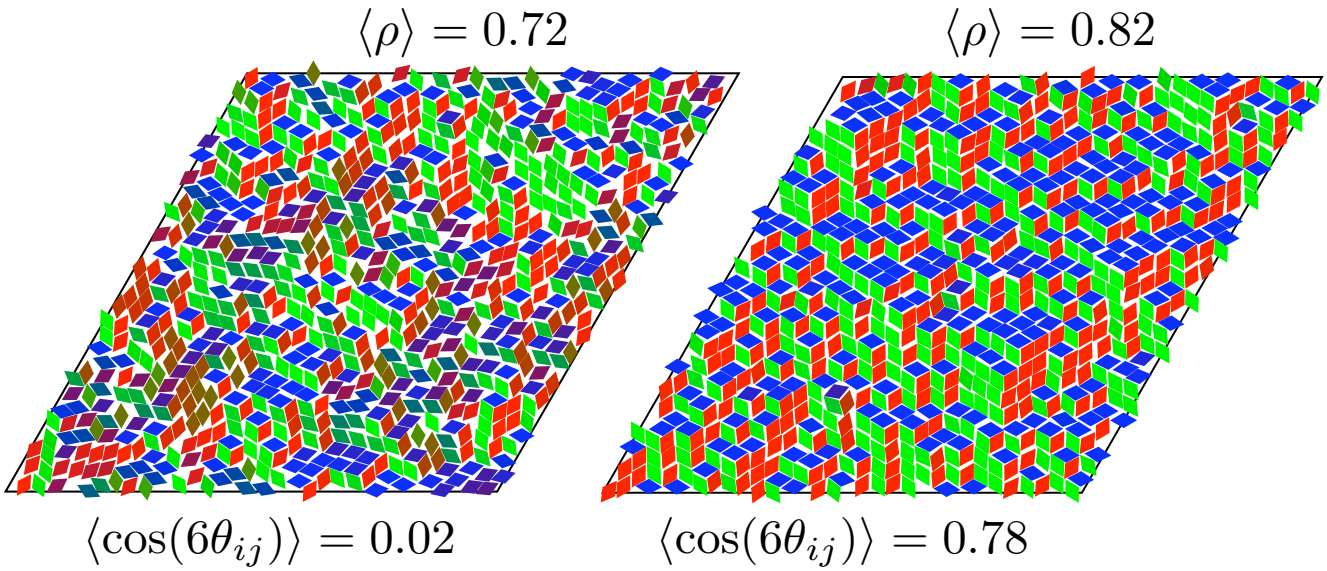


FIG. S2: Two simulation boxes of equilibrated regular rhombi. See Fig. 1, main text.

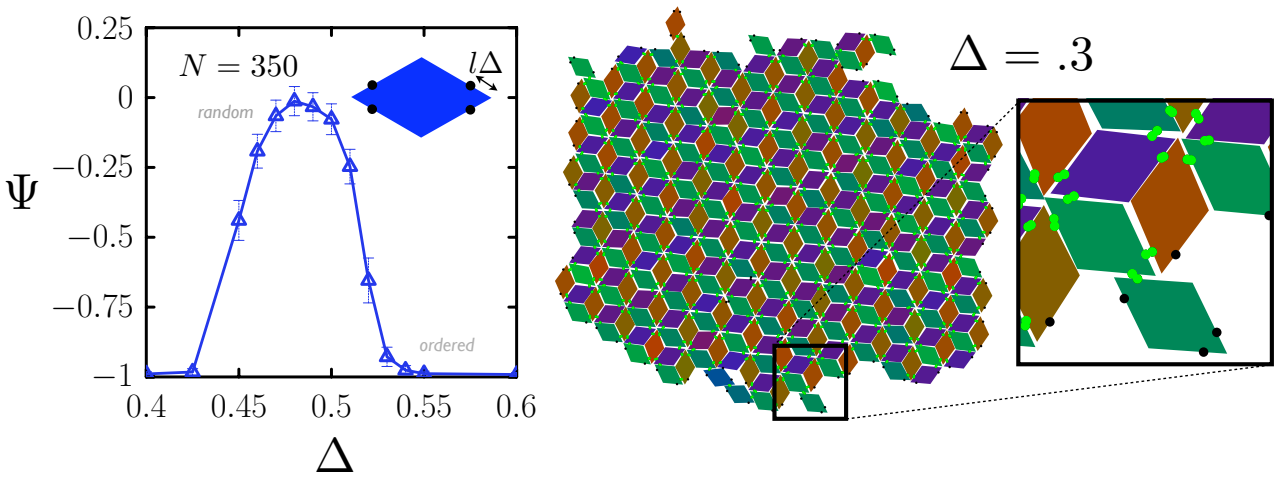


FIG. S3: Placing patches a fraction $\Delta$ between small- and large internal angles of the regular rhombus leads to self-assembly of the random tiling only close to the midpoint placement $\Delta = 1/2$. For large or small $\Delta$ the nonparallel mode of binding can still operate readily, but the parallel mode of binding becomes staggered (see snapshot), and cannot operate in a dense tiling. The least bias towards the nonparallel ordered phase is seen for patches shifted slightly towards the small internal angle ($\Delta \approx 0.48$). See Fig. 2, main text.

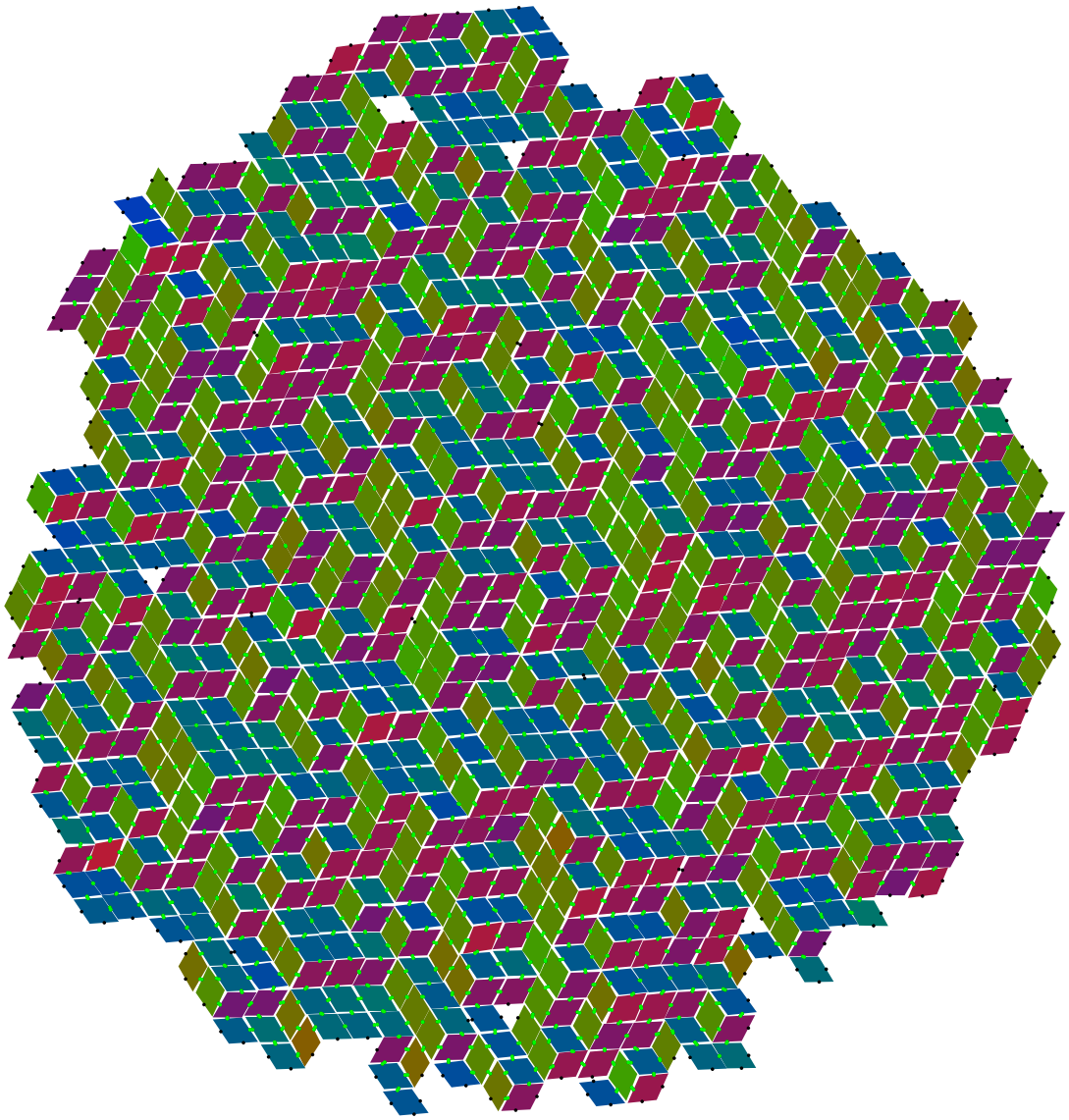

FIG. S4: Example of a tiling grown from regular rhombi. See Fig. 2, main text.

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