

# Broken symmetry and the variation of critical properties in the phase behaviour of molecular rhombus tilings

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The adsorption of dimers on periodic lattices, a paradigmatic problem in statistical mechanics<sup>1,2</sup>, is a well-known example of a physical system which can be mapped onto a non-periodic tiling of the plane. These systems have been studied theoretically for several decades<sup>3–6</sup> but the predicted random tiling phase has only recently been identified experimentally in a rhombus tiling formed by a supramolecular network<sup>7</sup>. Ideal random tilings are expected when there is an exact degeneracy between parallel and non-parallel alignment of neighbouring tiles. Here we show that when this degeneracy is broken, the asymmetric interactions between molecular tiles give rise to a rich phase diagram which can be explored experimentally. In particular, we observe both random tiled phases with critical properties which vary with the asymmetric interaction, and ordered phases dominated by either parallel or non-parallel tile alignment, in agreement with theoretical predictions<sup>8–11</sup>. Our results demonstrate that two-dimensional molecular networks support exotic tiling phases.

Two-dimensional molecular networks have great potential for the formation of surfaces with specific structural arrangements and functionalities<sup>12,13</sup>. Within the broad range of structures that have been explored, random molecular networks have gained considerable attention recently as exemplars of two-dimensional, nonperiodic glassy systems<sup>7,14,15</sup>. In this work we focus on molecular rhombus tilings formed at the liquid-solid interface following the deposition of solvated molecules of interest on highly-oriented pyrolytic graphite (HOPG) substrates. The resulting interfacial molecular networks are imaged using scanning tunnelling microscopy (STM) and the observed structures can be directly mapped to rhombus tilings. In-plane stabilisation of these molecular networks arises from hydrogen bonds formed between carboxylic acid groups<sup>16–18</sup>, resulting in two orientations of intermolecular bonding with the molecular backbone axes either parallel or non-parallel at 60°, as shown in Fig. 1a. To form a random tiling a close match between the two dimensions marked  $d_1$  and  $d_2$  in Fig. 1a is required. Examples of suitable molecules are *p*-terphenyl-3,5,3'',5''-tetracarboxylic acid (TPTC) (Fig. 1j), with  $d_1 = 8.7$  Å which we have studied previously<sup>7</sup>, and 1,4-diphenyl-1,3-butadiyne-3,3'',5,5''-tetracarboxylic

acid (DPBDTC) (Fig. 1i), with  $d_1 = 9.5$  Å synthesised specifically for this study;  $d_2 = 9.6$  Å for both molecules. To tile the plane perfectly a rhombus must have internal angles of 60° and 120°, a lozenge<sup>5</sup>, for which  $d_1 = d_2$ .

A random rhombus tiling is considered *ideal*<sup>8–11</sup> if the parallel and non-parallel tile alignments are degenerate. In this case the tiling configuration is determined solely by maximising configurational entropy. Such tilings possess no translational order and display correlations in tile orientation which have a logarithmic dependence on spatial separation, a signature of a ‘Coulomb’ phase<sup>3</sup>. However, if there is an energetic asymmetry,  $\Delta \equiv \varepsilon_N - \varepsilon_P \neq 0$ , where  $\varepsilon_N$  and  $\varepsilon_P$  represent non-parallel and parallel interaction energies, respectively, the degeneracy between the exponentially large number of tilings is broken. In this case an additional internal energy contribution to the free energy competes with the entropic term (rhombus tiles with asymmetric interactions are described as *interacting* in many theoretical models<sup>8–11</sup>). For small  $\Delta$ , random tiling phases (with critical orientational correlations which vary continuously with  $\Delta$ ) are expected, but large  $\Delta$  values are predicted to lead to transitions to ordered phases<sup>8–10</sup>. The parameter  $\Delta$  may be considered to be analogous to the coupling constant  $J$  which appears in Ising models of magnetism and leads to ordered phases for  $|J| \gtrsim k_B T$ , which may be either ferromagnetic or antiferromagnetic depending on the sign of  $J$ , while entropic terms in the free energy dominate for  $|J| \ll k_B T$  in which case a disordered paramagnetic phase occurs. Here we show for the first time that the rich phase behaviour predicted for rhombus tiles with asymmetric interactions may be investigated experimentally by preparing molecular arrays with differing values of  $\Delta$ .

Figures 1c to 1h show images of molecular networks prepared under several different conditions (see Methods), referred to as Experiments I to VI, respectively, and the corresponding rhombus tiling representations, where each molecule is represented by a rhombus coloured according to its orientation. To characterise our experimental tilings we define an order parameter,  $\psi = (n_0 p - p_0 n) / (n_0 p + p_0 n)$ , where  $n$  and  $p$  represent the fraction of rhombus tile junctions in non-parallel and parallel orientations, respectively, and  $n_0 \simeq 0.608$  and  $p_0 \simeq 0.392$  are the equivalent values for a defect-free, ideal, random tiling. As such,  $\psi = 1$  in a fully parallel phase,  $\psi = -1$  in a fully non-parallel phase, and  $\psi = 0$

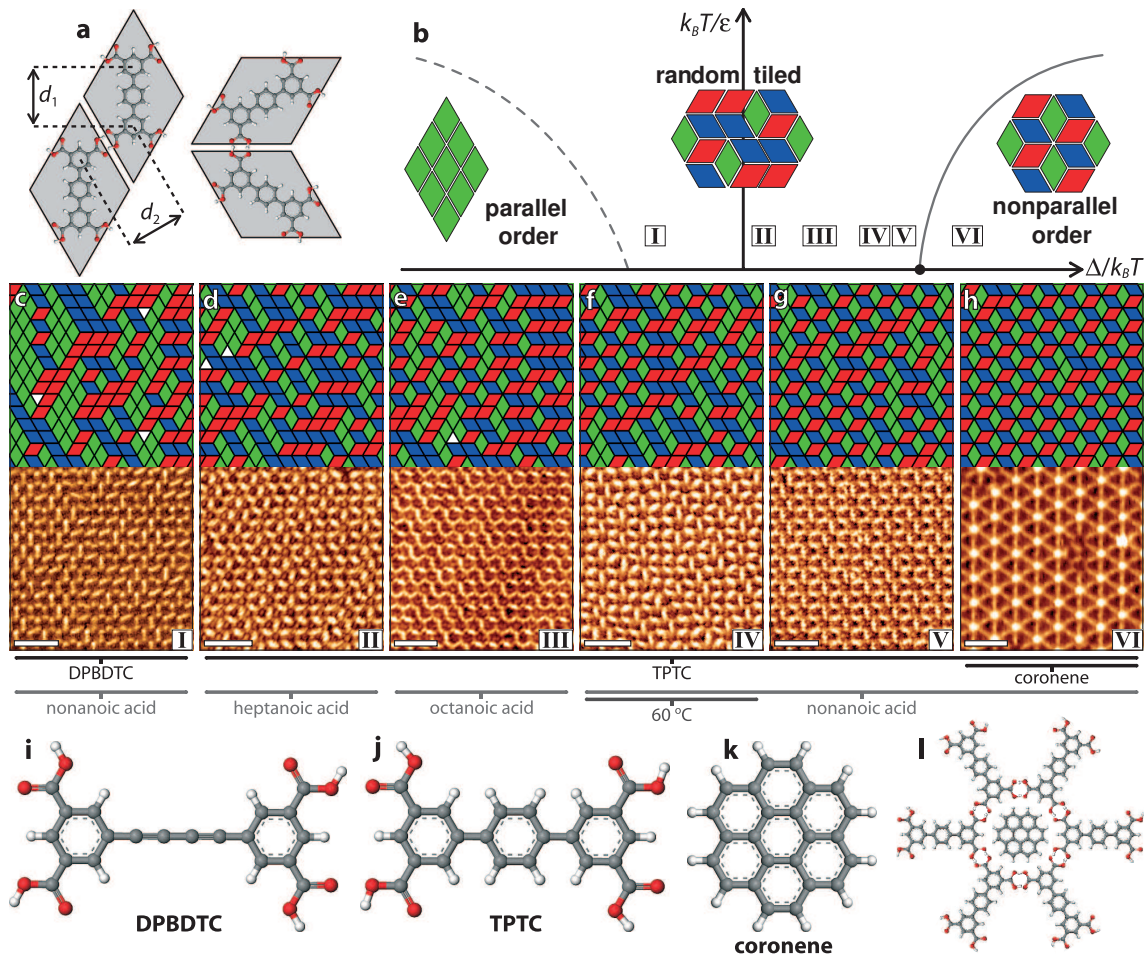


FIG. 1: **Tetracarboxylic acid supramolecular assemblies and rhombus tilings.** **a**, Parallel and non-parallel intermolecular bonding orientations, with backbone  $d_1$ , and bond,  $d_2$ , lengths indicated, overlaid onto the corresponding rhombus tile representations. **b**, Schematic phase diagram of the interacting rhombus tiling model as predicted by theory. Three phases are expected depending on the interaction energy  $\Delta$ : a random tiled phase with critical correlations for small  $|\Delta|$  (a so-called “Coulomb” phase), an ordered phase dominated by non-parallel bonding at large positive  $\Delta$ , and a second ordered phase dominated by parallel bonding at large negative  $\Delta$ . The transition between the random tiled and non-parallel ordered phases is expected to be continuous at  $T > 0$  (indicated by a full line in the sketch), and that to the parallel phase first-order (dashed line). **c-h**, STM images (sections of larger scans) of tetracarboxylic acid supramolecular networks at alkanolic-acid-HOPG interfaces and the corresponding rhombus tilings, in order of decreasing  $\psi$ . STM image contrast originates from molecular backbones (and, in **h**, coronene). All scale bars 50 Å, see Methods for imaging parameters. **i-k**, Molecular ball and stick diagrams of; **i**, DPBDTC; **j**, TPTC; and; **k**, coronene. **l**, Diagram of coronene adsorbed at the vertex of six TPTC molecules.

for an ideal tiling.  $\psi$  is calculated for each Experiment (I to VI), and the images (Figs. 1c to 1h) are placed in order of decreasing  $\psi$ , spanning  $\psi = 0.22$  to  $\psi = -0.68$ .

Fig. 1b is a schematic of the expected equilibrium phase diagram<sup>8-11</sup>. There are two relevant thermodynamic parameters: temperature,  $T$ , and energetic bias,  $\Delta$ . Ideal random tilings are observed for  $\Delta = 0$ . For  $\Delta > 0$  non-parallel bonding is favoured, resulting in increasingly negative values of  $\psi$ . For large enough  $\Delta$  the system orders into a crystalline phase dominated by non-parallel bonds. At  $T = 0$  this transition occurs at  $\Delta/k_B T \approx 0.45$  and is of the Kosterlitz-Thouless kind<sup>11</sup>, a type of transition which is only observed for two-dimensional systems (second order transitions do not

occur in 2D systems). For  $T > 0$  there is a finite concentration of tiling defects, spatial correlations in the random tiled phase have finite range, and the transition is continuous<sup>8</sup>. For  $\Delta < 0$  parallel bonding is favoured, resulting in increasingly positive values of  $\psi$ . The random tiled phase extends until  $\Delta/k_B T \approx -0.3$  where the system undergoes a first-order transition<sup>10</sup> to a crystalline phase dominated by non-parallel bonds. We reiterate the analogy with magnetic systems where transitions from disordered to ordered phases occur as the absolute value of the coupling constant is increased beyond some critical value.

It is clear from Fig. 1 that different experimental conditions give rise to tilings with varying degrees of order.

In Experiment I we investigated DPBDTC in nonanoic acid (Fig. 1c). For this arrangement there are more parallel bonds than expected for an ideal random tiling and  $\psi = 0.22$ . A solution of TPTC in heptanoic acid (Exp. II, Fig. 1d) results in a molecular tiling with  $\psi = -0.08$ . This is the molecular tiling closest to ideal (i.e.  $\psi = 0$ ) of all the systems we have studied. For TPTC a change of solvent<sup>21,22</sup> from heptanoic acid to octanoic (Exp. III, Fig. 1e,  $\psi = -0.25$ ) and nonanoic (Exp. V, Fig. 1g,  $\psi = -0.43$ ) acid, solvent molecules with similar chemistry but slightly larger size, leads to a progressive increase in the fraction of non-parallel bonds. Experiment IV is performed with TPTC and nonanoic acid at an elevated temperature of 60 °C (Fig. 1f,  $\psi = -0.35$ ). Comparing this molecular tiling with the equivalent tiling prepared at 19 °C (room temperature) we see that the increase in temperature leads, as expected, to a value of  $\psi$  closer to zero. Finally, the most negative order parameter,  $\psi = -0.68$ , is observed when coronene (Fig. 1k) is added to a solution of TPTC and nonanoic acid (Exp. VI, Fig. 1h). Coronene becomes incorporated in the molecular network in a site which enhances the stabilisation of the non-parallel arrangement (Fig. 1l), a capture process consistent with previous studies of coronene-carboxylic-acid and other systems<sup>23–26</sup>.

These results show that small modifications in experimental parameters lead to the exploration of the rhombus tiling model phase space. To determine the placement of the experimental structures on the phase diagram in Fig. 1b we have undertaken extensive numerical simulations of rhombus tilings. The details of the numerical scheme are provided in the Methods section and represent a generalisation of previous work<sup>19,20</sup> to the case  $\Delta \neq 0$ . Fig. 2a shows the numerically computed order parameter  $\psi$  as a function of scaled bias  $\Delta/k_B T$ . Vertical dashed and solid lines indicate where transitions from the random to the ordered phases occur. The six experiments are marked on the numerical curve according to their measured  $\psi$  values. Experiments II to V span the random tiled region with negative  $\psi$ ; Experiment VI lies beyond the phase boundary in the non-parallel phase; Experiment I is close to the phase boundary with the ordered parallel phase.

The numerical results in Fig. 2a provide a relationship between the order parameter  $\psi$  and  $\Delta/k_B T$  which allow an estimation of the latter for each of our experiments. Furthermore, using the known temperature at which the experiments were performed we can estimate values of  $\Delta$ , as tabulated in Fig. 2c. A comparison of Experiments IV and V is of particular interest: both were performed using TPTC in nonanoic acid but with molecular networks prepared at different temperatures. Accordingly we would anticipate the same value of  $\Delta$  and we find excellent agreement between the values inferred from simulations. This result provides strong support for our analysis and confirmation that the molecular arrays can be understood in terms of equilibrium structures. From our experiments it is clear that measurable variations in the

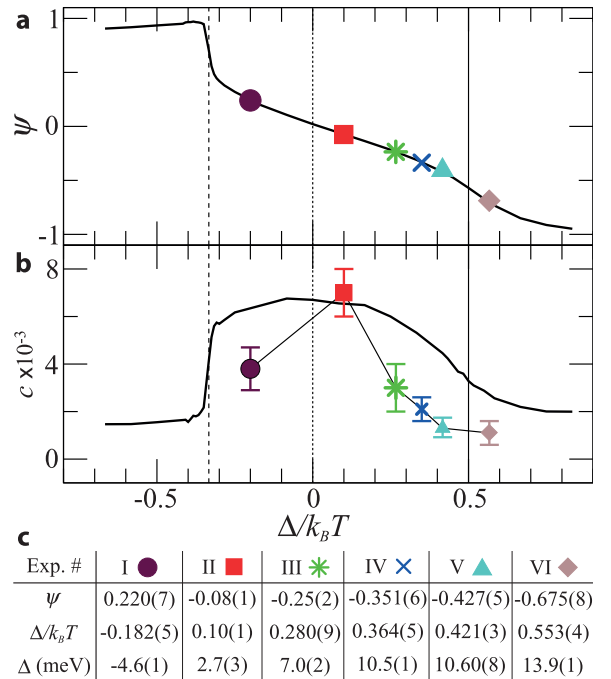


FIG. 2: Comparison of experiments to simulations of the rhombus tiling model. **a**, Order parameter  $\psi$  as a function of scaled bias  $\Delta/k_B T$ . The full curve is the result of numerical simulations of the rhombus tiling model (see Methods) for  $\varepsilon_N/k_B T = 5/3$  (at this value the concentration of defects  $c$  is comparable to that observed experimentally). The vertical lines indicate the approximate location of the continuous transition to the non-parallel ordered phase,  $\Delta/k_B T \approx 0.5$ , and the first-order transition to the parallel phase,  $\Delta/k_B T \approx -0.34$ . The experimental points are placed on the curve according to the measured values of  $\psi$ . **b**, Concentration of defects as a function of bias. The full curve is the numerical result. The abscissa values for experimentally measured defect concentrations are fixed by panel **a**: the experiments show the predicted non-monotonic dependence on bias. **c**, Estimate of bias  $\Delta$  for the six experiments. Notice that  $\Delta$  for Experiments IV and V, which correspond to the same system (TPTC in nonanoic acid) at different temperatures, is the same within experimental error, as expected.

tiling statistics may be identified even for variations of  $\Delta$  of  $\lesssim 5$  meV, much less than the thermal energy at room temperature.

A second experimental measure, which can also be compared with numerical results, is the concentration of defects. These ‘half-rhombus’ vacancies are topological defects and are present in several of the images shown in Fig. 1. For an ideal tiling their concentration,  $c$ , has been shown to depend on temperature<sup>19</sup> (we choose an effective temperature in our simulations to match, approximately, the maximum defect density observed in experiments) and we show in Fig. 2b that  $c$  is also controlled by  $\Delta$ . We highlight the non-monotonic dependence on bias which results from the strong suppression of isolated triangular defects in the ordered phases. The experimentally-determined defect data is plotted against

the theoretical curve using the value of  $\Delta/k_B T$  obtained from Fig. 2a. We note that the non-monotonic behaviour and suppression of defect formation in the ordered phases is reproduced in our data providing further support of the validity of our approach to determining the value of  $\Delta$  for our experiments.

Rhombus tilings are commonly analysed as a projection of the interface of a simple cubic lattice onto a (111) plane<sup>3</sup>. In this approach each vertex is assigned an effective height  $h(x, y)$  ( $x$  and  $y$  are the co-ordinates of the vertex) using a simple procedure (outlined in Fig. 3j). An analysis of our images using this approach shows explicitly the difference between the random and ordered phases as shown in Fig. 3. Here we show larger area images for Experiments I, IV and VI, in three different representations. The first is the tiling representation, as in Fig. 1 (Figs. 3a, 3d, and 3g). The second representation is given by the height map  $h(x, y)$  (Figs. 3b, 3e, and 3h): Experiment I shows a clear height gradient, Fig. 3b, indicative of its closeness to the phase boundary to the parallel phase; in contrast the height maps for Experiments IV and VI, Figs. 3e and 3h, show averaged height gradients which are close to zero. This is expected for both the random and non-parallel ordered phase although these can be distinguished by the larger height fluctuations present for Experiment IV consistent with a random tiling phase.

The third representation illustrates the spatial variation of non-parallel order. In a perfectly non-parallel configuration the unit cell (e.g. see schematic inset of Fig. 1b) can be centred at any of the three sub-lattices of the triangular lattice. Choosing a sublattice is the symmetry breaking associated with the transition to the non-parallel phase and in general we would expect to observe domains of non-parallel order corresponding to each of these three possible sub-lattices. Again a magnetic analogue is useful; in a ferromagnetic system domains of spin-up and spin-down magnetisation are formed whose size diverges as the system undergoes a transition from a paramagnetic to a ferromagnetic phase. For the case considered there are three equivalent non-parallel ordered states into which the system can crystallise, rather than the two states available for a simple magnetic system. In Figs. 3c, 3f, and 3i regions of non-parallel aligned tiles are coloured cyan/yellow/magenta depending on their assignment to one of the three possible non-parallel phases. For Experiment I, Fig. 3c, these domains are relatively small since the parallel tile alignment predominates. The domains are larger but finite for Experiment IV, Figs. 3f, in the random tiling phase. For Experiment VI, Fig. 3i, one domain has become dominant and is comparable with the size of the system, indicative of a transition to the non-parallel phase.

Our results show conclusively that the phase space of two-dimensional rhombus tiles which arises from asymmetric interactions, may be explored experimentally through the structural characterisation of molecular arrays. The changes in energy which give rise to different

ordering are small compared to the thermal energy, an essential requirement for systems where entropy is significant. It is likely that the simple characteristic energies in our model include contributions from solvent-molecule, molecule-substrate and solvent-substrate interactions. The role of solvent molecules is complex and their co-adsorption on the surface with the molecular networks is likely to lead to small changes in the relative stability of parallel and non-parallel structures. Energy differences on this scale are beyond the confidence levels normally associated with modern numerical approaches to molecular modelling (e.g. density functional theory, molecular dynamics) and the inclusion of solvent molecules makes a detailed microscopic description and prediction of energies particularly problematic. However our experiments give clear limits on the tolerance of the random tiling phase to symmetry breaking - a difference in binding energies of  $\gtrsim 10\text{meV}$  will drive the structures into an ordered phase.

Our study demonstrates that prototypical self-assembled systems such as supramolecular networks can reveal a richness of exotic phases which have been studied widely by theorists and are analogous to those found in complex condensed-matter systems. In addition our work highlights the role of entropy in the balance between order and disorder in molecular templates.

## Methods

**Chemicals.** 1,4-diphenyl-1,3-butadiyne-3,3',5,5''-tetracarboxylic acid (DPBDTC) and *p*-terphenyl-3,5,3'',5''-tetracarboxylic acid (TPTC) were synthesized in-house, details of their synthesis can be found in the accompanying Supplementary Material and Ref. 7 respectively. Other chemicals used were coronene ( $\geq 95.0\%$ , Fluka), heptanoic acid ( $\geq 97\%$ , Sigma), octanoic acid ( $\geq 98\%$ , Aldrich), and nonanoic acid ( $\geq 95\%$ , Fluka).

**STM experiments.** STM images were acquired with an Agilent Technologies 4500 PicoPlus STM using a PicoScan controller and STM tips formed from mechanically cut PtIr (80:20) wire. Saturated solutions of the desired adsorbate (DPBDTC or TPTC) were prepared by placing an excess of solid in the desired solvent (heptanoic, octanoic, or nonanoic acid). For Experiment VI, the solution used combined equal volumes of a saturated solution of TPTC in nonanoic acid and coronene in nonanoic acid (conc.  $1.5 \times 10^{-4}$  mg/mL). All solutions were ultrasonically agitated to ensure complete dissolution. To form the supramolecular networks, a  $10 \mu\text{L}$  droplet of solution was deposited onto a mechanically cleaved HOPG substrate. Imaging at the alkanolic-acid-HOPG interface commenced immediately after approach of the STM tip. For Experiment IV, the substrate was heated to  $60^\circ\text{C}$  prior to solution deposition and held at this temperature for the duration of the experiment. Figure 1 STM imaging parameters ( $V_{tip}/I$ ): 1c, +1.1 V/10 pA; 1d, +1.2 V/15 pA; 1e, +1.2 V/5 pA; 1f,

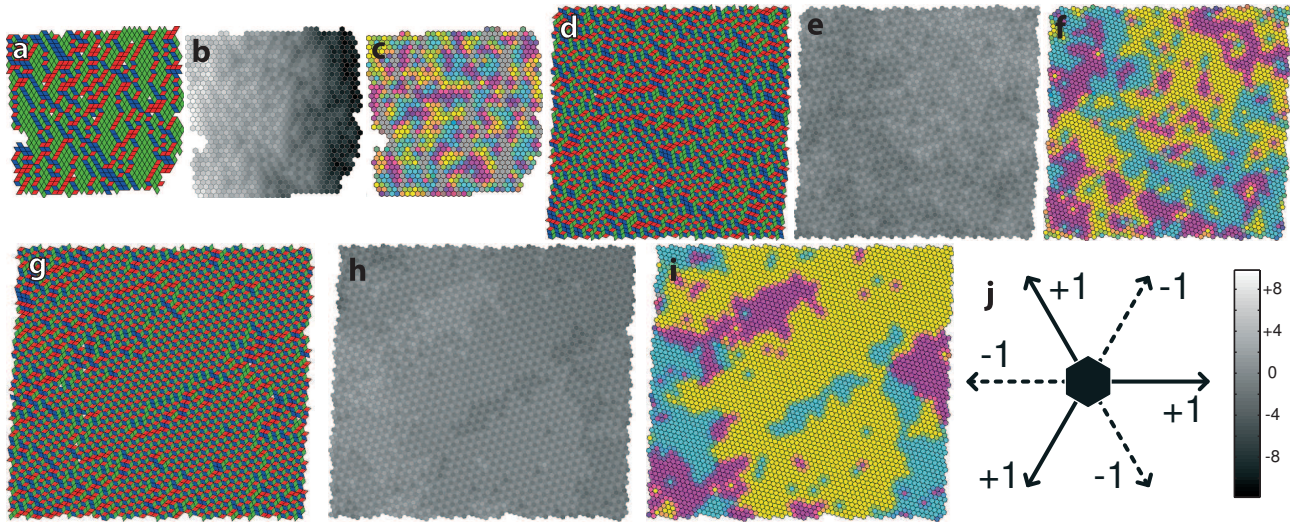


FIG. 3: **Ordered phase analysis of tetracarboxylic acid supramolecular networks.** **a-c**, Experiment I (DPBDTC in nonanoic acid): **(a)** tiling representation of a 50 nm STM image; **(b)** height field representation, showing that at this scale the system is ‘tilted’; **(c)** non-parallel phase domain representation (we colour cyan/yellow/magenta the three possible different sub-lattice arrangements of the non-parallel ordered phase). **d-f**, Experiment IV (TPTC in nonanoic acid): **(d)** tiling representation (80 nm image), **(e)** height field representation; **(f)** non-parallel phase domain representation. **e** and **f** show that the structures of Experiment IV are neither tilted, nor display any significant non-parallel phase order, as expected of a random tiling. **g-i**, Experiment VI (TPTC and coronene): **(g)** tiling representation (100 nm image); **(h)** height field representation; **(i)** non-parallel ordered domain map. While **h** shows that the structure is overall flat, **i** shows that one ordered non-parallel domain has become prevalent indicating a spontaneous breaking of symmetry due to a transition to the ordered non-parallel phase. **j**, Scheme for calculating the height field: moving along the edges of tiles the field  $h(x, y)$  increases/decreases by the amounts indicated.

+1.25 V/12 pA; 1g, +1.0 V/13.5 pA; 1h, +1.0 V/30 pA.

**Numerical simulations.** We simulated rhombus tilings on the lattice using the same model as in Ref. 19 supplemented by interactions which varied depending on whether neighbouring tiles were parallel (binding energy  $\epsilon_P$ ) or non-parallel (binding energy  $\epsilon_N$ ). Simulations were performed with continuous time Monte Carlo which allows to access very long times at low temperatures (i.e. very low number of defects) on systems sizes between  $N = 18^2$  to  $99^2$  and averaged over  $10^3$  samples for each state point. The location of the continuous transition from the random tiled to the ordered non-parallel phase at  $T \neq 0$  (the location at  $T = 0$  is known exactly<sup>11</sup>) was determined from finite size scaling analysis of susceptibilities and higher order cumulants of  $\psi$  and of the ‘columnar’ order parameter (difference in density of non-

parallel order in each sublattice) as in Ref. 8; the location of the first-order transition to the ordered parallel phase from the jump in  $\psi$  and the ‘tilt’ order parameter (difference in density of each kind of tile), cf. Ref. 10.

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