Deriving molecular bonding from macromolecular self-assembly

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Abstract

Macromolecules can form regular structures on inert surfaces. We have developed a combined empirical and modeling approach to derive the bonding. From experimental scanning tunneling microscopy (STM) images of structures formed on Au(111) by melamine, by PTCDA, and by a 2:3 mixture of the two, we determine the molecular bonding morphologies. Within these bonding morphologies and recognizing the distinction between cohesive and adhesive molecular interactions we simultaneously simulated different molecular structures using a lattice Monte Carlo method. Within these bonding morphologies there is a distinction between cohesive and adhesive molecular interactions. We have simulated different molecular structures using a lattice Monte Carlo method.

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Self-assembly of molecules on atomically well-defined surfaces offers a bottom-up approach for generating two-dimensional nanostructures [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14]. To develop structures for specific purposes requires a precise knowledge of the molecular bonding, including molecular binding rules and the corresponding binding energies [15, 16]. These cannot always be calculated ab initio because of the complex character of molecular bonding and the difficulty of including dispersive (van der Waals) interactions [17].

Hydrogen bond-forming molecules are particularly suitable for generating self-assembled structures due to the high selectivity and directionality of hydrogen bonds [19, 20, 21], and relatively low energetics which enable equilibrium molecular configurations to be achieved at relatively low processing temperatures [8, 18]. Using mixtures of different hydrogen bond-forming molecules, with diverse binding rules, [22, 23] allows the formation of a wider variety of molecular structures by changing molecular composition, and presents a promising approach to generating molecular scaffolds [24]. The relation between the properties of individual molecules and the characteristics of their self-assembly on surfaces remains to be understood. Our study provides a step towards establishing such a relation by solving the inverse problem - extracting characteristics of molecular interactions by analysing self-assembled structures.

In this paper we use experimental observations of a self-assembled molecular structure to determine plausible binding rules, and then perform kinetic Monte Carlo simulations to estimate the binding energies. We analyse simultaneously the structural stability of the stoichiometric molecular mixture and the individual constituent molecular components. We apply this methodology to PTCDA and melamine molecules on Au(111), where the substrate has little effect on intermolecular interactions.

Our procedure for extracting the molecular binding rules and the corresponding interaction energies involves two major steps. In the first step we analyse experimentally observed molecular
structures in order to extract the characteristics of the molecular arrangement for all molecular compositions of interest. Thereby we identify the ways molecules bind to each other, i.e. the molecular binding rules. In the second step we construct the model system using the binding rules and arranging the molecules on a grid, suitable for on-lattice kinetic Monte Carlo simulations of molecular structures. Thereby we extract the molecular binding energies by analysing simultaneously the stability of both the single-component molecular structures and of that formed from a binary mixture.

We used Au(111) film grown on mica substrates. The samples were introduced into the ultrahigh vacuum (UHV) chamber of a STM (JEOL JSTM4500S) operating at a pressure of $10^{-8}$ Pa. The Au(111) surfaces were sputtered with argon ions and annealed in UHV at temperatures between 600 and 800 °C typically for 30 min. PTCDA molecules were sublimated at 275 °C and melamine at 100 °C. Electrochemically etched tungsten tips were used to obtain constant current ($I_t$) images at room temperature with the bias voltage ($V_s$) applied to the sample. The structures of molecular mixture was obtained after deposition of PTCDA on Au(111), followed by a deposition of melamine with a 2:1 ratio and a post annealing at 90 °C for 10 hours.

Molecular binding rules between identical molecules are obtained by comparing the molecular arrangements in the single-component molecular structures. The experimental images of the molecular structures of 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) and 1,3,5-triazine-2,4,6-triamine (melamine) self-assembled on Au(111) are shown in Fig. [1]. Fig. [1] shows the compact domains of PTCDA, which exhibit a uniform structure with a herringbone-like pattern. The $12.0 \times 20.0 \, \text{Å}^2$ unit cell of the structure is rectangular and contains two molecules with their main axes oriented at an angle of 86 ° with respect to each other [25]. Molecular bonding in the PTCDA structure can be characterized by two independent parameters $E_{pp}^{(1)}$ and $E_{pp}^{(2)}$ as illustrated in Fig. [1g] and 1h, respectively. Melamine molecules on Au(111), according to Fig. 1d,
FIG. 1: (a-c) PTCDA domain: a) STM-image on Au(111) surface (14×10nm²; V_s = +1.5 V, I_t = 0.4 nA), b) simulation result displayed on a sheared hexagonal lattice, c) molecular ordering. (d-f) Melamine domain: d) STM-image (14×10nm²; V_s = -1.0 V, I_t = 0.5 nA), e) simulation shown on a simple hexagonal lattice, f) molecular ordering. The unit cell is outlined in blue. (g,h,i) Plausible molecular bonds occurring in structures c and f. In the molecule 3D representation, gray balls are carbon atoms, red balls are oxygen atoms, white balls are hydrogen atoms and blue balls are nitrogen atoms.

Form domains of chiral structure and hexagonal symmetry with the lattice parameter of 9.8 Å. This arrangement is stabilized by a double hydrogen bond [26], as illustrated in Fig. 1i. The corresponding energy $E_{mm}$ for the melamine-melamine bonding is found to be $E_{mm} = 0.45$ eV [27].

Details of the melamine-PTCDA molecular bonding are obtained by analysing the structure of the melamine-PTCDA mixture with the composition 2:1. This large scale structure is formed of ordered molecular stripes, as shown in Fig. 2a. Each stripe is composed of a single PTCDA molecular row and a double row of melamine molecules, Fig. 2b. The PTCDA molecular axis is rotated by 50° with respect to the stripe line thereby making this structure chiral. The unit cell outlined in Fig. 2b in blue has a parallelogram shape, with an angle of 85° with 10.0 Å (the periodicity along the PTCDA rows) and 19.9 Å parameters (PTDCA-PTCDA separation across
FIG. 2: Mixed PTCDA and melamine domain. (a) STM-image on Au(111) surface (80×60nm²; Vₛ = -1.2 V, Iₜ = 0.2 nA), (b) Close up (14×8 nm²; Vₛ = -1.5 V, Iₜ = 0.1 nA), (c) simulation result shown on a sheared hexagonal lattice, (d) model of the molecular ordering, (e-f) plausible molecular bonds occurring in d.

2 melamine rows). Fig. 2d shows the molecular arrangement as observed in Fig. 2b. Molecular interactions in the PTCDA-melamine structure can in general be characterized by two parameters E⁽¹⁾ₘₚ and E⁽²⁾ₘₚ corresponding to physically reasonable hydrogen bonding as illustrated in Fig. 2e,f.

The molecular binding energies E⁽¹⁾ₚₚ, E⁽²⁾ₚₚ, E⁽¹⁾ₘₚ and E⁽²⁾ₘₚ can now be estimated by studying the stability of the self-assembled single-components and the mixed molecular structure using the kinetic Monte Carlo methodology [27] with an underlying hexagonal grid defining the topology of molecular movements and interactions and an (N,V,T) ensemble.

The on-lattice kinetic Monte Carlo model is an entirely topological model. It exclusively considers binding energies between molecules that are nearest neighbours in the underlying lattice, and does not contain information about the absolute position and orientation of molecules. Therefore the point of comparison between experimental and simulated structures is the topological
FIG. 3: Simulated PTCDA-melamine ordering depending on PTCDA-melamine bond energies $E_{mp}^{(1)} = E_{mp}^{(2)} = E_{ad}$, varying from 0.1 eV to 0.275 eV. (a,b) Small bond energies between PTCDA and melamine with $E_{ad} \leq 0.175$ lead to a phase segregation. (c,d) In a narrow energy range of 0.2 $\leq E_{ad} \leq 0.225$ melamine double rows can be observed as a typical defect. (e-f) Energies $E_{ad} \geq 0.25$ allow the formation of a defect-free PTCDA-melamine domain.

FIG. 4: The double melamine row in an PTCDA-melamine domain. (a) close-up of an STM image (8×8nm$^2$; $V_s = -1.2$ V, $I_t = 0.2$ nA). (b) Scheme showing the common topology of both experiment and simulation. Red rectangles are PTCDA molecules and blue triangles are melamine molecules. (c) Simulated image using a simple hexagonal geometry.
correspondence (Fig. 4). The freedom to apply different geometries to a simulation while keeping
the topology unchanged can be used for visualisation of highly ordered homogeneous molecular
arrangements (Fig. 1, Fig. 2), where a sheared hexagonal geometry achieves a good correspon-
dence. In other cases where the geometry is more complex due to defects or irregularities (Fig. 3,
Fig. 4), the simulation is presented with a simple hexagonal geometry. In each case, what matters
is the correspondence in topology between simulation and experiment.

In our simulations we use a binary mixture of anisotropic molecules of type 1 (trigonal vertices)
and type 2 (linear rods) occupying one and two sites, respectively, on a $30 \times 30$ two-dimensional
hexagonal lattice, initialized in a random configuration. Rod-like molecules exist in three different
orientations along the symmetry axes of the hexagonal grid, while vertex-like molecules exist in 2
different orientational configurations, due to their two-fold and three-fold molecular symmetry, re-
respectively. Any pair of molecules that exists in one of the nearest neighbour configurations, shown
in Fig. 1k,h,i and Fig. 2 e,f, establishes a hydrogen bond with the energies $E_{mm}$, $E_{pp}^{(1,2)}$, $E_{mp}^{(1,2)}$, respectively. The number of molecules (200 vertices, 100 rods) is chosen to be stoichiometric,
complying with the ratio of the experimentally observed unit cell shown in Fig. 2. The simulation
temperature of $k_B T=0.08$ eV is higher than in experiment to enable short equilibration times, but
low enough to avoid thermally generated defects.

In our simulations we neglect the influence of the substrate on the molecular binding ener-
gies, which is a reasonable approximation for the PTCDA and melamine molecules on Au(111)
[28]. The structure of the molecular mixture can be unstable against phase separation into single-
molecular domains. This instability is controlled by the strength of the cohesive interactions asso-
ciated with $E_{pp}^{(1)}$ and $E_{pp}^{(2)}$ relative to the adhesive interactions associated with $E_{mp}^{(1)}$ and $E_{mp}^{(2)}$. This
trade-off can be simplified by assuming that $E_{pp}^{(1)} \approx E_{pp}^{(2)} = E_{coh}$ and $E_{mp}^{(1)} \approx E_{mp}^{(2)} = E_{adh}$, reducing the
number of fit parameters down to two.
In Fig. 1 and Fig. 2 we show the predicted structures with high symmetry molecular ordering in order to compare with the illustrated experimental images. The pure PTCDA domain in Fig. 1b and the pure melamine domain in Fig. 1e are both the result of the binding rules and the high enough binding energies to ensure thermal stability of the structures. The stability of the PTCDA-melamine structure requires a certain range of adhesive interaction energies for given values of the cohesive interaction energies, as illustrated in Fig. 3.

In Fig. 3a-f we show how the structure undergoes a change, caused by varying the PTCDA-melamine interaction strengths $E_{mp}^{(1)}=E_{mp}^{(2)}=E_{ad}$. We observe that values of $E_{ad} = 0.175$ eV, $E_{coh} = E_{pp}^{(1)}=E_{pp}^{(2)} = 0.15$ eV lead to the phase separation due to the weak PTCDA-melamine interactions. Whereas $E_{ad} = 0.2$ eV creates structures with long range ordering and a sporadic but reproducible occurrence of double melamine row defects. Fig. 4 highlights that these double row defects in the PTCDA-melamine domains are observed in STM (Fig. 2a and Fig. 4a) and are also predicted by our simulation (Fig. 4c). It can be seen from Fig. 4b that both experiment (Fig. 4a) and simulation (Fig. 4c) correspond topologically. Reproducing the double-row defect in our simulations allows the range for the effective energy parameters to be narrowed as given in Table 1.

The interaction energy values we found allow all three experimentally observed structures shown in Fig. 1 and Fig. 2 to be simulated simultaneously, as illustrated in Fig. 1b, e, and Fig. 2c. The obtained energies $E_{ad}$ and $E_{coh}$ comprise the contributions from both the hydrogen bonds and van der Waals interactions. The latter energies are usually in the range 0.04-0.1 eV [17], which is around the lower limit of the variation range identified for the parameters $E_{ad}$ and $E_{coh}$. Hence the major contribution to the obtained values of $E_{ad}$ and $E_{coh}$ can be associated with the hydrogen bond energies.

By combining STM images of molecular ordering in a PTCDA-melamine system with on-lattice Monte Carlo simulations of the structural stability we have determined the molecular bind-
TABLE I: Summary of binding rules and energies in the PTCDA-melamine system. Abbreviation: mm=(melamine-melamine), pp=(PTCDA-PTCDA) and mp=(melamine-PTCDA).

| Type | Bond type    | Energy            | Arrangement | Energy range                |
|------|--------------|-------------------|-------------|----------------------------|
| mm   | $2 \times \text{N} - \text{H} \cdots \text{O}$ | $E_{mm} = 0.45 \text{eV}$ | $[27]$      | reference value             |
| mp$^{(1)}$ | \text{N} - \text{H} \cdots \text{O} | $E_{mp} = E_{adh} = 0.225 \text{eV}$ | $0.2 \text{eV} < E_{adh} < 0.25 \text{eV}$ |
| mp$^{(2)}$ | \text{N} - \text{H} \cdots \text{O} | $E_{mp} = E_{adh} = 0.225 \text{eV}$ | $0.2 \text{eV} < E_{adh} < 0.25 \text{eV}$ |
| pp$^{(1)}$ | $2 \times \text{C} - \text{H} \cdots \text{O}$ | $E_{pp} = E_{coh} = 0.15 \text{eV}$ | $0.1 \text{eV} < E_{coh} < 0.3 \text{eV}$ |
| pp$^{(2)}$ | $2 \times \text{C} - \text{H} \cdots \text{O}$ | $E_{pp} = E_{coh} = 0.15 \text{eV}$ | $0.1 \text{eV} < E_{coh} < 0.3 \text{eV}$ |

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