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Molecular Packing and Symmetry of Two-Dimensional Crystals

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ABSTRACT

Periodic arrangements on surfaces resulting from monolayer formation are critical in determining the electronic structure of thin films, the adhesion of surface coatings, the properties of lubricants, and the polymorphic form of heteronucleated crystals. Unlike substrate-directed chemisorption, the process of physisorption is highly responsive to molecular structure and stands out as a controllable method of creating variable surface patterns with periodicities on the low end of the nanoscale. Despite decades of study focused upon such ordered structures, the principles guiding the formation of these two-dimensional crystals have been obscured by the lack of a systematic and critical compilation. Thus, *prediction* of two-dimensional structure based upon the composition of the individual building blocks remains in its infancy. Here we demonstrate through the compilation and analysis of a database of two-dimensional structures that molecular-scale patterns are dictated by the same factors that determine bulk crystal structure, but these factors give rise to different preferred packing symmetries. In marked contrast to three-dimensional systems, achiral molecules in two-dimensional crystals are likely to adopt chiral structures, and racemic mixtures are expected to produce enantiopure domains. The determination of plane group frequencies allowed experimental verification of Kitaigorodskii's 50-year old theory of close packing as applied to two-dimensional tiling. This fundamental comparison between bulk crystals and physisorbed monolayers provides new tools and directions for future exploration in the engineering of surfaces with prescribed two-dimensional patterns.

Introduction

Self-assembly through physisorption at surfaces is a ubiquitous phenomenon of intense fundamental and technological importance. A variety of molecule types self-assemble in this manner, including metal−organic coordination networks,[1] nanoparticles,[2,3] and organic molecules.[4,5] Monolayer structure in the early stages of deposition affects the electronic and optical properties of thin films[6] and directs the structure of heteronucleated crystalline solids.[7,8] The properties of polymeric and oligomeric surface coatings and lubricants are often dominated by the assembly process at the substrate interface.[9] Even systems on much larger length scales, such as those of biological importance, are influenced by two-dimensional packing,[10,11] as are the self-assembled structures of nanoscale objects used as masks for lithography.[12] Despite the impact of structure on the properties of these assemblies, the study of two-dimensional crystals has been limited to a case-by-case basis, making it difficult to discern shared behavior and establish generalizations and expectations.

A critical analysis of monolayers observed by scanning tunneling microscopy (STM) at the liquid−solid interface was conducted and the data were assembled into a resource dubbed the Two-Dimensional Structural Database (2DSD). The 2DSD provides the unified view of interfacial self-assembly essential for investigation of two-dimensional crystallization and comparison with bulk crystals to uncover the basic similarities underlying all forms of self-assembly and the differences due to the presence of an interface; an important caveat is that most studies cataloged have been carried out on a single substrate (see Database Construction and Scope and Supporting Information for selection criteria, structural assignment, and a discussion of potential sources of bias). This compilation is a two-dimensional analogue of the three-dimensional crystal structure databases the Cambridge Structural Database (CSD)[13] and the Protein Data Bank (PDB).[14] These resources initiated the field of crystal engineering and revolutionized study of bulk self-assembly by providing statistical information on crystal packing, including symmetry relationships and identification of structure-determining intermolecular interactions that are difficult to discern in isolated cases.[15−19] Crystal packing in three dimensions is dominated by the satisfaction of strong intermolecular interactions and the drive toward close packing, which involves energy minimization through reducing void space;[16] the 2DSD can be employed to explore the effect of these factors on two-dimensional crystal packing. The tendency toward close packing in two dimensions has been invoked in explanations of the structures of individual two-dimensional crystals[20] but until now without a means to test its general applicability. Confirmation of this tendency has been particularly overdue considering that the cornerstone for understanding bulk assembly, the theory of close packing, was

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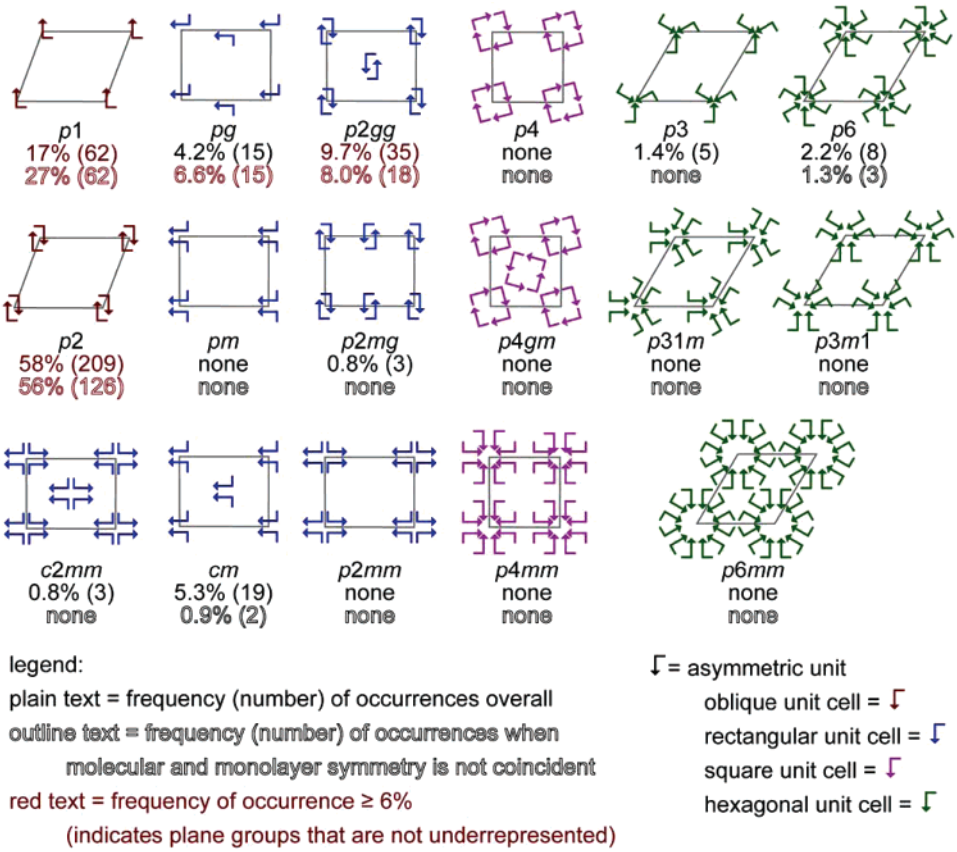

FIGURE 1. Schematic representation of the 17 plane groups used to describe monolayer symmetry for entries in the 2DSD. An arrow indicates each asymmetric unit, and unit cells are denoted with gray lines. Plane group frequencies of all unique entries in the 2DSD of sufficient resolution are given, followed by a parenthetical listing of total number of occurrences and number of occurrences where molecules are not located on a symmetry element.

developed from examination of hypothetical two-dimensional packing symmetries almost 50 years ago.[21]

For each entry in the 2DSD, a structural description that matched the STM image was developed (see Database Construction and Scope and Supporting Information) including the plane group,[22] the number of molecules in the asymmetric unit, and the symmetry element on which the molecule resides. A plane group is one of 17 different combinations of the symmetry elements (translation; 2-, 3-, 4-, and 6-fold rotations; and glide and mirror planes) that fill two-dimensional space (Figure 1). When some number of molecules or fractions of molecules, the asymmetric unit, is combined with the symmetry elements from the plane group, the observed monolayer packing is reproduced (Figure 2).[23] Many substances exist as two or more crystalline phases with different arrangements and/or conformations of molecules in the lattice, and each of these pseudopolymorphs[24−26] were given a separate entry. Of the 876 total monolayers included in the database, a subset of 359 unique examples (supplied in the Supporting Information) was selected for the detailed analysis presented here based upon the quality of the data.

Results and Discussion

The observed preference for a few plane group symmetries out of numerous possibilities in the structures of two-dimensional crystals (Figure 1) is analogous to the space group preference apparent in the crystal structures of organic and metallo-organic compounds. A handful of three-dimensional space groups, $P2_1/c$ (35.6%), $P\bar{1}$ (22.5%), $P2_12_12_1$ (8.3%), $C2/c$ (7.8%), and $P2_1$ (5.6%), describe the vast majority of the crystal structures in the CSD (see Supporting Information), while all other groups have an occurrence rate of less than 5%. These large percentages are remarkable when it is noted that, if crystal structures were equally occurring in all 230 space groups, no one group would account for more than 0.5% of entries. These common space groups are those that allow densest packing and hence maximize the intermolecular interactions for arbitrary shapes or shapes with inversion centers.[21] In two dimensions, the plane groups *p*1, *p*2, *pg*, and *p2gg* enable objects of any shape to contact the largest number of neighboring objects, providing 6-fold coordination. The principle of close packing posits that denser structures are favored; hence, these plane groups are predicted to be preferred. Indeed, the most commonly occurring plane groups in the 2DSD were *p*2 (58%), *p*1 (17%), and *p2gg* (9.7%) (Figure 1). Together, these three groups account for 85% of the structures. If we compare this to the hypothetical situation where each of the 17 plane groups are equally likely, then any group accounting for more than 6% of entries (approximately 20 entries given the current size of the dataset) can be considered overrepresented. From this view, the plane groups *p*1 and

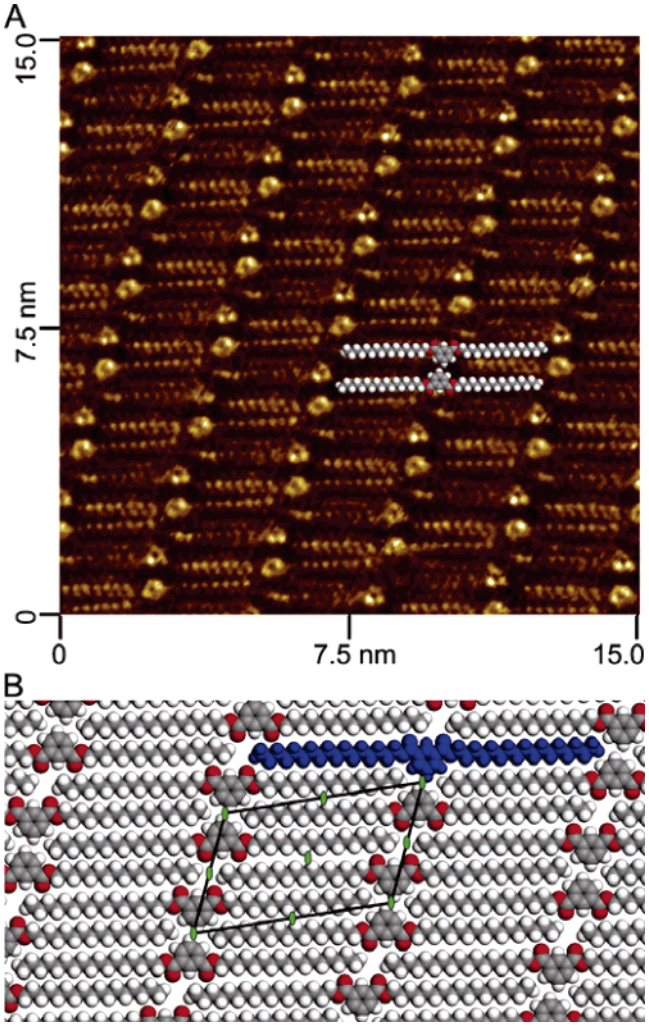

FIGURE 2. An example of the symmetry analysis carried out for two-dimensional crystals in the 2DSD. (A) An STM image of 1,3-diheptadecylisophthalate with an overlaid model of two molecules.[20a] Large bright circles correspond to the aromatic rings and small bright spots adopting a zigzag pattern are due to hydrogen atoms attached to the alkyl chains, indicating that the carbon backbone is parallel to the surface. (B) A model of the packing with the unit cell (black outline), asymmetric unit (blue molecule), and symmetry elements (2-fold rotations are represented by green ovals) indicated. The 2DSD entry is assigned a plane group of *p*2; the asymmetric unit consists of one molecule that does not sit on a symmetry element, although the isolated molecule contains mirror planes and a 2-fold rotation.

*p*2 are overrepresented by 3 and 10 times, while 12 of the 17 plane groups are underrepresented by at least a factor of 2 and usually much more. The overall plane group frequencies are affected by the coincidence of molecular and monolayer symmetry, but this effect is removed when the dataset is restricted to those crystals where molecules are not sitting on a symmetry element. In this subset, only *p*2 (56%), *p*1 (27%), *p*2*gg* (8.0%), and *pg* (6.6%) are observed in substantial numbers and all others are underrepresented, with two groups observed at far lower rates and the remaining 11 groups not observed at all. Thus, the theory of close packing as applied to two-dimensional tiling has at last been experimentally verified and demonstrated to act upon the whole of a general class of materials. Regardless of whether self-assembly occurs at interfaces or in bulk, the structures are, in general, influenced by the tendency toward minimization of empty space.

This similarity is particularly striking given the differences in the chemical makeup of the datasets from the 2DSD and the CSD. The CSD contains a greater variety of molecule types than the 2DSD, which is largely made up of molecules with long alkyl chains. Neither the chemical nature of these molecules nor the presence of the substrate induced deviation from the drive toward minimization of empty space.

Observations outlined so far indicate that certain plane groups will be preferentially obtained over the entire class of assemblies. However, the particular type of molecule, with its associated functionality, can influence the likelihood of particular monolayer symmetries. Thus, establishing connections between the molecular properties and the monolayer symmetry is essential for the design of monolayers of specific symmetry and metrics. Monolayer symmetry is often generated that is greater than molecular symmetry (46% of entries). This production of symmetry elements can result from the satisfaction of specific intermolecular interactions, indicating that supramolecular synthons may be employed in two dimensions as they have been used in three dimensions.[27] The entries in the *p*6 plane group consisting of molecules not residing on a 6-fold rotation resulted from the judicious placement of hydrogen-bonding groups to produce a 6-fold symmetric clusters of molecules.[28−30] Further examples of the correlation between some functional groups and particular symmetry elements are apparent in the 2DSD. Molecules with carboxylic acid groups generate 2-fold rotations (79% of occurrences) when dimerized, and hydroxyl groups often generate glide planes (44% of occurrences).

Although the drive toward close packing is shared between two- and three-dimensional crystals, it has different implications for the chirality of these systems. Inversion centers are the most favored symmetry elements in three dimensions, regardless of whether the molecule resides upon them, because as point operations they generate the least amount of surrounding empty space and minimize the like−like interactions that interfere with close packing.[16] The propensity toward formation of inversion centers, dictated by close packing in bulk crystals, leads to a preference for centrosymmetric space groups. This means that when achiral molecules crystallize, they generally adopt achiral space groups,[31,32] and when crystals are formed from racemic mixtures, unit cells that consist of both enantiomers are usually produced. Furthermore, crystals that contain both enantiomers in the unit cell tend to be denser, an observation known as Wallach's rule,[33] and more stable[34,35] than their enantiopure counterparts. In a plane, 2-fold rotations, which are the projection of inversion centers onto two-dimensional space, provide closest packing. Although inversion centers do require less space than 2-fold rotations, they are generally incompatible with interfacially formed two-dimensional crystals because of the inherent noncen-

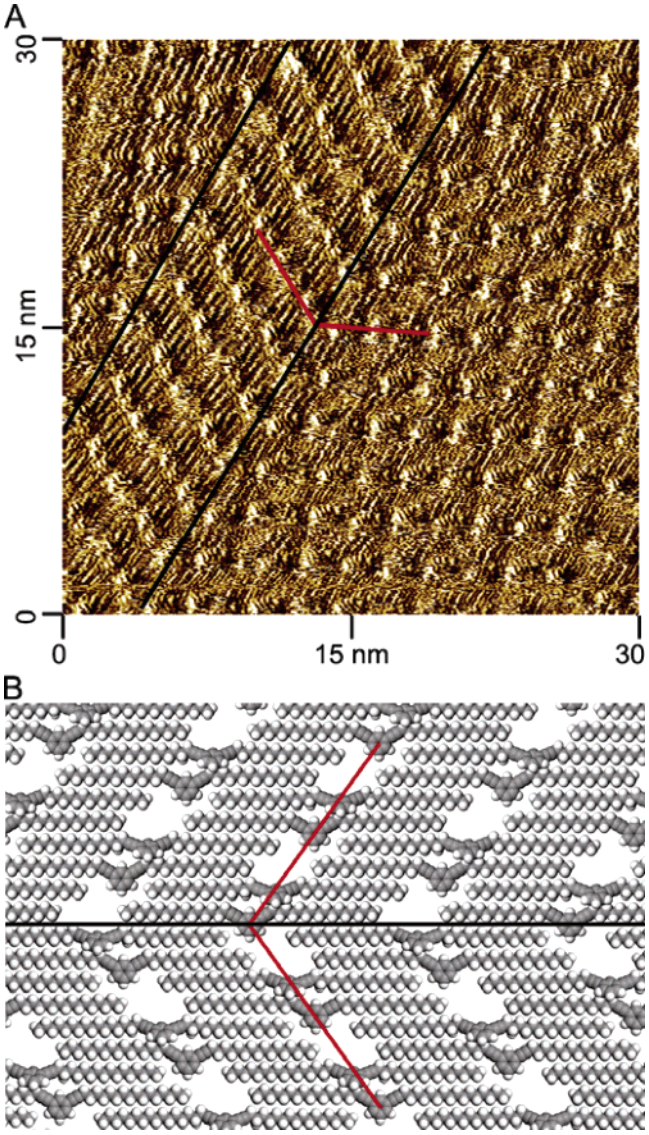

FIGURE 3. An example of a polycrystalline chiral monolayer illustrating coexisting enantiomorphous domains resulting from two-dimensional crystal formation by an achiral molecule. (A) An STM image of 1,3-dioctadec-1-ynylbenzene.[20a] The large bright features correspond to pairs of aromatic rings. The bright lines extending to both sides of these features are the alkyl chains. (B) A model of the packing illustrating an interface between two domains. In both figures, black lines indicate crystalline domain boundaries of enantiomorphous domains, and red lines denote the mirror-related column propagation directions.

trosymmetricity at interfaces.[36] This propensity for 2-fold rotations in packing motifs on a surface and the dearth of mirror planes, which produce empty space and therefore hinder close packing, predicts a preference for chiral crystal formation. Indeed, this is verified by the predominance of plane groups *p*2 and *p*1, which are both chiral plane groups, meaning that mirror-related, non-superimposable domains can be formed on the surface (Figure 3). Glide planes do enable close packing and produce achiral plane groups, but the groups *pg* and *p2gg* are observed much less frequently than *p*1 and *p*2. This is analogous to the case of three-dimensional crystals, where screw axes offer close packing in chiral space groups, but

Table 1. Retention of Various Symmetry Elements from the Molecular Symmetry in the Monolayer Packing

symmetry element present in molecule	total no. of occurrences	no. of occurrences of element retention in monolayer	% retained
2-fold	185	104	56
3-, 4-, or 6-fold rotation	37	15	41
mirror	376	21	5.6

symmetries with screw axes alone are nevertheless adopted much more rarely than symmetries with inversion centers. Taking into account all of the chiral plane groups, *p*1, *p*2, *p*3, *p*4, and *p*6, 79% of structures in the 2DSD are chiral, even though the vast majority of these are built from achiral molecules. This preference for formation of chiral monolayers stands in striking contrast to three-dimensional crystals, where structures in chiral space groups make up only 19% of the CSD and most of these are crystals grown from enantiomerically pure compounds.[16] The tendency toward two-dimensional chirality means that most adsorbed molecules, regardless of the presence or absence of inherent stereochemistry, will likely form enantiomerically pure domains. Indeed, it has been noted repeatedly in experimental studies that both achiral molecules[37−39] and racemic mixtures form segregated, mirror-related domains at achiral surfaces.[40−43] This difference cannot be explained by a variation in the percentage of chiral symmetry groups between two and three dimensions, because the relative proportion of these groups is similar. While five out of 17 plane groups are chiral (29.4%), there are 65 chiral space groups of the 230 possible (28.2%).[44] Thus, if all chiral groups were selected from with equal probability, there would be little discrepancy between the frequency of occurrence of chirality in two- and three-dimensional crystals. This behavior is instead a consequence of close packing in two dimensions being most commonly satisfied in the chiral plane groups *p*2 and *p*1. This is a fundamental finding, but it has important practical consequences. For example, chiral interfacial structures, which are commonly generated due to this preference for chiral crystal formation in two dimensions, have been observed to induce formation of enantioenriched oligomers[45] and produce crystals that vary in orientation with respect to the interface by inducing face-selective nucleation.[42]

Although the relationship between molecular and ensemble properties is not straightforward in either two- or three-dimensional packing, analysis of the 2DSD finds relationships between the symmetry elements present in the molecule and their retention in the crystalline packing. The tendency toward close packing affects the rates of molecular symmetry retention for various elements; therefore, in the design of monolayers, the symmetry elements present in the molecules can be employed to influence the packing symmetry. Two-fold rotations, the symmetry elements most compatible with the closest-packing plane groups for any shape, are commonly kept in the monolayer symmetry (Table 1). Mirror planes, however, produce

like−like interactions that are detrimental to close packing and are generally lost in the two-dimensional assembly. This is analogous to bulk crystals, where the preferred inversion centers are commonly retained while mirror planes are not.[16,46] Mirror planes are even more likely to be lost in two dimensions, as molecules often adsorb such that they are parallel to the surface. In two dimensions, molecules that have 3-, 4-, or 6-fold rotational symmetry, symmetry elements that require an intermediate amount of open space when packing in a plane, form monolayers that retain these symmetry elements in less than half of occurrences. Knowledge of the preference for retention of some elements and not others enables generalizations to be made about crystal packing and suggests pathways for and constraints on the purposeful design of crystals expressing prescribed two-dimensional symmetry.

Of the 17 possible plane groups, eight have not yet been observed to occur. These missing plane groups are highly symmetric, involving higher-order rotations (*p*4, *p*4*gm*, *p*4*mm*, *p*3*m*1, *p*31*m*, and *p*6*mm*) and mirror planes (*pm* and *p*2*mm*). Although a few space groups make up the majority of three-dimensional crystal structures in the CSD, essentially all of the 230 groups have been observed at least once,[47] unlike the two-dimensional crystals in the 2DSD. This is probably due to the insufficient diversity of reported compounds, rather than the impossibility of obtaining many of these packing symmetries. Induction of these high-symmetry groups will depend on molecular properties such as symmetry and intermolecular functional group interactions, as suggested above. Engineering the missing highly symmetric surface patterns represents a formidable challenge that will test and expand upon the relationships observed above. The statistical analysis of two-dimensional crystals can be employed to address many other aspects of interfacial self-assembly, such as the influence of the substrate on symmetry retention or the effect of molecular chirality on packing symmetry, although a greatly expanded dataset will be necessary. Not only are more two-dimensional crystal examples needed but also expanded discussion and reporting of monolayer structure and cell constants in the literature.

Conclusion

The compilation of the 2DSD represents a critical step toward systemization of the field of two-dimensional crystallization and a unified treatment of self-assembly. Just as the CSD revolutionized the study of molecular crystals by facilitating structural analysis across a diverse array of examples, the 2DSD should enable a greater understanding of fundamental surface phenomena. Such understanding will facilitate a new field of surface engineering: the design of nanoscale-patterned surfaces with specified metrics, symmetry, and functionality. Controlling interfacial self-assembly opens the possibility of designing the properties of films and bulk structures from the earliest stages of crystallization, providing new avenues for the production of functional materials.

Analysis of the 2DSD has enabled a number of otherwise unattainable measurements. The determination of the plane group frequencies reveals a marked preference for a few groups among the many possible, indeed the same groups predicted by the principle of close packing. Thus, the fundamental drive toward dense packing that has been long established to affect the structure of bulk crystals has finally been experimentally confirmed to affect the packing symmetry for interfacial assemblies arising through physisorption. The preference for particular plane groups also provides an explanation for the repeatedly noted phenomena of chiral two-dimensional crystal formation by achiral molecules and spontaneous resolution at surfaces by racemic mixtures: observations that have previously been met with surprise are now revealed to be an expected consequence of close packing expressed in two dimensions. In addition to plane group frequencies, relationships between the symmetry and functionality of molecules with the two-dimensional packing motif adopted have been established. Symmetry elements are retained in two-dimensional crystals at rates that are dependent on the compatibility with close packing. Particular strong interactions can induce monolayer symmetry greater than that of the molecule, suggesting that supramolecular synthons can be employed to control two-dimensional crystal packing as they have been in three dimensions. These observations suggest avenues for the design and control of monolayer structure by variation of molecular properties.

Database Construction and Scope

Dataset Selection. A tractable and self-consistent subset of two-dimensional crystals was sought, in which the packing motif is highly responsive to the nature of the adsorbed molecule and where a dynamic equilibrium exists, favoring the formation of the thermodynamically most stable monolayers. Thus, although the definition of a two-dimensional crystal can encompass a variety of structures that have periodicity in two dimensions, we restrict ourselves here to those observed to physisorb at the liquid−solid interface. Only monolayers observed by STM were chosen, because the submolecular resolution provided is essential for symmetry assignments. Just as in the CSD and the PDB, the dataset of the 2DSD is biased in that it is limited to compounds that have been deemed of sufficient interest to warrant study and reporting and are able to be crystallized and characterized with the given method.

The vast majority of monolayers meeting the above criteria were observed on highly oriented pyrolytic graphite (HOPG); thus, for initial statistical determinations only graphite substrates were included. HOPG is particularly amenable to ambient-condition STM imaging, due to the stable, atomically flat surface that is readily obtained by cleavage. Most of the included monolayers exhibited similar behavior with regard to the substrate. Generally, there was alkyl chain alignment with the graphite lattice, resulting in domains related by 120° angles and with

structures typically commensurate or coincident.[48] Monolayer structure and registry with the graphite may vary considerably for closely related molecules.[20a] Thus, while substrate−adsorbate interactions make a large contribution to the stability of the monolayer, it is the adsorbate−adsorbate interactions that are critical in selecting between possible packing motifs that would similarly satisfy interaction with the substrate. The differences in adsorption energies at various surface sites on graphite are very small and routinely overcome by the intermolecular interactions between adsorbed molecules at room temperature according to enthalpy calculations.[49] The graphite substrate certainly affects the structure of the monolayers; different substrates often produce different packing motifs for the same molecule.[50−54] One anticipated effect of the highly symmetric graphite substrate is an increased observation of symmetric plane groups that have 3- and 6-fold rotations. On the basis of the few published comparisons, packing motifs on HOPG tend to be more symmetric than those seen on gold,[50,51] but highly symmetric groups are still underrepresented in the 2DSD dataset.

Several classes of two-dimensional crystals were excluded from the present analysis to control for exterior influences that have a dramatic impact on structure. Chemisorbed self-assembled monolayers, which have structures more directly arising from covalent attachment to the substrate, were excluded. Only monolayers imaged at the solution-solid interface by STM without additional applied potential were included. Applied potential has a powerful affect on the crystalline structure adopted at the surface, causing switching among multiple packing motifs,[55,56] and therefore, it must be explored independently. Structures produced by Langmuir−Blodgett methods require the additional consideration of applied pressure when identifying the root cause of selection of a particular packing arrangement. This is another variable that is best studied independently. Only monolayers of monodisperse species were included, excluding polydisperse metal clusters and polymers, because of the reduction in periodicity that results from random incorporation of differently sized components into a monolayer. Physisorbed monolayers formed by evaporation of solvent and by vacuum sublimation were excluded from the 2DSD because of the increased likelihood of observing a metastable state that accompanies these nonequilibrium deposition methods.

Structure Assignment. For each of the selected monolayers, a number of symmetry assignments that are generally lacking from the original literature were made. Due to the variation in registry of the monolayer with respect to the substrate and the infrequency with which this relationship was quantified for published images, the structural assignments describe the overlayer only. The maximum possible point symmetry of the molecule was identified, with a preference for higher rotational symmetry. The plane group symmetry,[22] crystal class, number of molecules in the unit cell (Z), and number of molecules in the asymmetric unit of the monolayer (Z'), as well as the symmetry element upon which the molecule sits were assigned. These symmetry assignments were derived from the STM images, complemented by molecular models. The Supporting Information contains details of the assignments, a complete list of assignments for the data presented here, and a list of references for all monolayers included in the 2DSD.

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Supporting Information Available: Details of database construction and structural assignment, expanded discussion of selection criteria, a table comparing the symmetry of the position on which a molecule sits in the unit cell to the highest possible molecular symmetry, a table of space group frequencies, a list of all of the references included in the 2DSD, and the structural assignments for cited entries in the 2DSD. This material is available free of charge via the Internet at http://pubs.acs.org.

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