

# On the Formation of Ordered Two-Dimensional Molecular Assemblies

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The concept of *commensurability of intraassembly planes* is developed and its importance in the formation of stable two-dimensional molecular assemblies is discussed. It is argued that it is not enough to examine the matching of cross-sectional areas of different molecular parts ( $S_m$ ). Thus, it is important to consider the crystallographic mismatch of intraassembly atomic planes when designing molecular materials based on Langmuir-Blodgett or self-assembled monolayers. Finally, it is argued that even with  $S_m$  match and a given epitaxy, we still have the bond between these molecular parts to worry about.

## Introduction

Understanding of the interrelationships between the molecular structure of chainlike molecules and their organization in layered aggregates is still a fundamental problem.<sup>1</sup> Examples include Langmuir monolayers at the air-water interface, Langmuir-Blodgett (LB) films, self-assembled (SA) monolayers, lipid membranes, liquid crystals, and molecular crystals. The common feature to these systems is the presence of two-dimensional structures with varying degrees of translational and orientational order. The two-dimensional ordering within these planes results mainly from intermolecular interactions such as van der Waals and electrostatic interactions.<sup>2-5</sup> In simple amphiphiles, the strength of intermolecular interactions has been suggested to be a function of the spacing between the molecular head groups.<sup>6,7</sup>

We have argued previously<sup>1</sup> that the advance of molecular materials depends upon the capacity of materials scientists to develop thin films with optimized properties and a high degree of ordering. We have envisioned self-assembly as a method by which we can provide solutions to this problem and develop the capacity to design organic films with predicted architectures and properties.<sup>8-10</sup> That molecules will spontaneously form a stable close-packed layer is vital to the success of any material design based on the SA—or for that matter LB—approach. Of further importance is the ability of complex molecules to form two-dimensional assemblies with long-range order, preferably in monodomain macroscopic films. We have discussed before, the problems in the molecular packing and ordering when a bulky group—usually a rigid, planar  $\pi$ -system—is incorporated into a long alkyl chain (Figure 1).<sup>1</sup> This is because the bulky group disrupts the pseudohexagonal close packing, thus increasing the in-

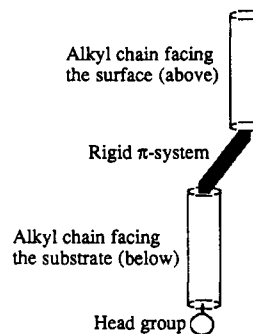


Figure 1. A schematic description of an amphiphile containing a  $\pi$ -system.

tramolecular dihedral energy.<sup>11</sup> The discussion above cannot be completed without mentioning that the question of what is the minimum number of molecules needed to form a stable cluster is still unresolved. This is a fundamental one when considering devices based on molecular materials.

The idea that three-dimensional molecular crystals can be viewed and analyzed as an assembly of commensurate two-dimensional molecular layers has been developed in recent years by one of us.<sup>12</sup> In this paper, we take this idea one step further, develop the broader concept of *commensurability of intraassembly planes*, and discuss its importance in the formation of stable two-dimensional molecular assemblies. We suggest that it is not enough to examine the matching of cross-sectional areas ( $S_m$ ) of different molecular parts—as usually is the practice in the design of amphiphilic molecules. Thus, while matching of  $S_m$  is necessary, it is not sufficient. At the next level of complexity, it is also important to consider the *crystallographic commensurability* of the different atomic layers *within* the assembly when designing molecular materials based on LB or SA monolayers. Finally, we argue that even with a  $S_m$  match and a given epitaxy, we still have the bond between these molecular parts, i.e., the valence geometry, to worry about.

## Discussion

Let us start from a simple planar  $\pi$ -system, e.g., tetrathiafulvalene (TTF), tetracyanoquinodimethane (TCNQ), naphthalene, biphenyl, etc.

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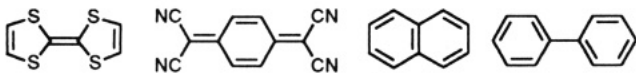
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Such  $\pi$ -systems tend to aggregate spontaneously in layers, usually with herring bone structures (Figure 2). Paraffins ( $C_nH_{2n+2}$ ) also spontaneously assemble in layer structures, which can be viewed as pseudo-hexagonally close-packed. In both cases there usually is more than one possible stable packing arrangement, and in some cases these different arrangements may have about the same stabilization energy.<sup>12</sup> This, for example, is the case for hydrocarbon chains, where both straight and tilted structures are stable and depend upon the nature of the terminal groups (Figure 3). Thus, in long-chain alcohols and dialkylbenzene derivatives, the chains are tilted by  $+30^\circ$  or  $-30^\circ$  with respect to an axis normal to the lamella, while in many alkanes and fatty acids they are not. This has recently been confirmed by Rabe and Buchholz using scanning tunneling microscopy (STM).<sup>13</sup>

If the planar, rigid  $\pi$ -system and the alkyl chain are bonded chemically to form one molecule, it is not clear a priori if this molecule also will assemble spontaneously in a layered structure. For example, it has been established that LB films of alkyl TCNQ derivatives have a "mosaic structure", in other words, they are nothing but a collection of crystallites.<sup>14</sup>

In trying to understand the factors that determine formation of layered structures of complex molecules, we begin by discussing the  $S_m$  mismatch of the two molecular parts. Let us assume that the cross-sectional area of one molecular part (e.g., the alkyl chain, 1) is  $S_m(1)$  and that of the second part (e.g., TCNQ, 2) is  $S_m(2)$ . Then the condition  $nS_m(1) = mS_m(2)$  should be satisfied. In other words, there should exist integers  $n$  and  $m$  that satisfy this cross-sectional area relationship. For example, if  $m = 2n$ , it means that two alkyl chains have to be attached to 2 for a stable two-dimensional assembly to be formed. Indeed, this has been demonstrated recently by Naito et al. who studied LB film assemblies of TTF, TCNQ, and other rigid  $\pi$ -systems substituted by a steroid skeleton. They clearly showed that when the cross-sectional areas of the alkyl chains (or of the steroid moiety) and that of  $\pi$ -system match, stable, condensed, and homogeneous LB films are formed.<sup>15</sup>

This condition, however, is not enough, and if only the  $S_m$  mismatch condition is satisfied, films with short range crystallographic order will be formed. Therefore, the second condition should be that the intraassembly planes—that of the layered 1 moieties and that of the layered 2 moieties—will be commensurate, i.e., an epitaxial matching of the sublattices. Hence, if  $\mathbf{a}_1$  and  $\mathbf{b}_1$  are the lattice vectors associated with the layer of 1 (of course,  $S_1 = (\mathbf{a}_1 \times \mathbf{b}_1) \cdot \hat{n}$ , where  $S_1$  is the area of the layer cell of 1, and  $\hat{n}$  is the layer normal), and  $\mathbf{a}_2$  and  $\mathbf{b}_2$  are the lattice vectors associated with the layer of 2 moieties, then the following relationships will define epitaxy of these intraassembly layers

$$N\mathbf{a}_1 = n_1\mathbf{a}_2 + n_2\mathbf{b}_2$$

and

$$M\mathbf{b}_1 = m_1\mathbf{a}_2 + m_2\mathbf{b}_2$$

where  $n_1$ ,  $n_2$ ,  $m_1$ ,  $N$ , and  $M$  are integers. In other words, for the molecule to form spontaneously stable two-

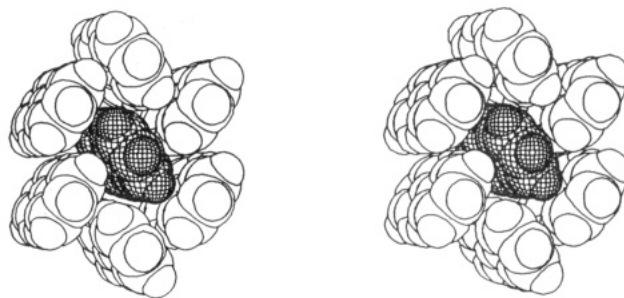


Figure 2. The  $ab$  layer of a biphenyl crystal structure in  $P2_1/a$ .

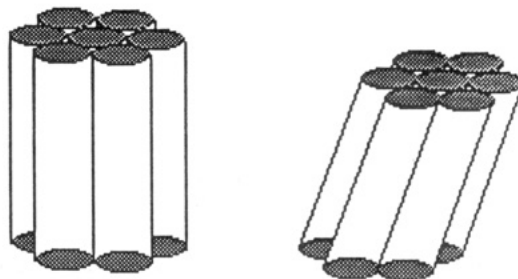


Figure 3. A schematic description of straight (left) and tilted (right) paraffin chains.

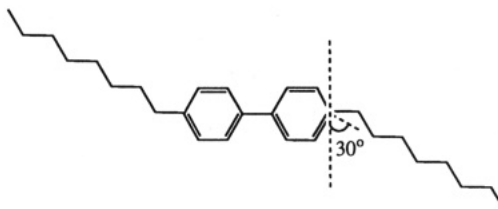


Figure 4. 4,4'-Dioctyl-1,1'-biphenyl.

dimensional aggregates, it is essential that the incommensurability of the intraassembly planes will be very small.

An analysis to determine compatibility of molecular parts is very difficult. In principle, one must have a method of determining all possible close-packed layer-cells for each fragment and then compare the results for possible epitaxial relationships. As an elementary, but important, example, consider the 4,4'-dialkyl-1,1'-biphenyl (Figure 4). For simplicity, we assume that the only possible close-packed layer for biphenyl is represented by the  $ab$  layer of its crystal structure in  $P2_1/a$  (Figure 2). For the alkyl fragments, it is well-known that all possible close-packings can be derived from the subcell concept.<sup>16</sup> Given that the biphenyl layer cell is rectangular, we consider only the packings that can be derived from rectangular alkyl subcells,  $O_\perp$ ,  $O_\perp'$ ,  $O_\parallel$ , and  $O_\parallel'$ . Lattice constants for these are given by Abrahamsson et al.<sup>17</sup> and in Table I. In addition to the layers with the same lattice dimensions as the subcell, one also expects that if any alkyl chain is shifted along the chain axis an integral number of times by  $c_s$  (2.54 Å), the new packing will differ from the original only in the position of the end groups. Clearly, given this

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**Table I.** Lattice Constants for the Paraffin Layer and for the Biphenyl Layer

packing symbol	tilt direction	$n^a$	cell, Å		$S_c, \text{Å}^2$	$S_m, \text{Å}^2$	tilt angle, deg
			a	b			
$O_\perp$			4.97	7.48	37.2	18.6	0
$O_\perp(a)$	a	1	5.58	7.48	41.7	20.9	27
$O_\perp(b)$	b	2	4.97	9.04	44.9	22.5	34
$O_\perp'$			7.43	5.01	37.2	18.6	0
$O_\perp'(a)$	a	2	9.0	5.01	45.1	22.5	34
$O_\perp'(b)$	b	1	7.43	5.62	41.8	20.9	27
$O_\parallel$			9.15	9.22	75.14	18.8	0
$O_\parallel(a)$	a	2	9.60	9.22	88.5	22.1	32
$O_\parallel(b)$	b	2	8.15	10.53	85.8	21.5	29
$O_\parallel'$			7.93	4.74	37.6	18.8	0
$O_\parallel'(a)$	a	2	9.41	9.74	44.6	22.3	33
$O_\parallel'(b)$	b	1	7.93	5.14	40.8	20.4	23
biphenyl			5.64	8.12	45.8	22.9	0

<sup>a</sup> Number of methylene shifts between molecules related by translation along the tilt direction (see refs 16 and 21 for details).

<sup>b</sup> Surface area of unit cell.

process, the local environment of the internal  $\text{CH}_2$  units will remain unchanged. Apparently, this idea was forwarded as early as 1938.<sup>18</sup> If one takes lattice symmetry into account, then entire rows of alkyl chains are displaced by one methylene unit in unison, resulting in a new set of lattice constants in which the chains are tilted relative to the layer normal by 25–35°. Indeed, such tilted alkyl packings are observed even in systems as simple as the crystalline paraffins  $\text{C}_{28}\text{H}_{58}$ <sup>19</sup> and  $\text{C}_{36}\text{H}_{74}$ .<sup>20</sup> A complete set of cell constants for tilted alkyl packings has been given by Kitaigorodsky.<sup>21</sup> In Table I we give results for a rectangular cell only, with tilt angles.

Examination of Table I shows that none of the tilted alkyl layers achieves  $S_m$  as large as that observed for biphenyl, but each, in fact, allows for one packing with a  $S_m$  within 0.4–0.8 Å<sup>2</sup> of that for biphenyl. Therefore, on this basis, the surface area mismatch is not large. However, for these tilted cells ( $O_\perp(b)$ ,  $O_\perp'(a)$ ,  $O_\parallel(a)$ , and  $O_\parallel'(a)$ ), no approximate epitaxial relationship with biphenyl is evident. For  $O_\parallel(b)$ , we have  $a_p \approx b_b$  and  $b_p \approx 2a_b$  (where subscript p represents paraffins and b represents biphenyl), the match for the second relation being 11.28 vs 10.53 Å, which results in the low  $S_m$  of 21.5 Å<sup>2</sup> for the alkyl layer.

The discussion developed above suggests that the organization of ordered two-dimensional assemblies of complex molecules requires the formation of an ordered, *segregated* layer, which implies that both sublayers should be in a close-packed low-energy arrangement. This condition can be fulfilled only if the bond between these molecular parts does not perturb the  $S_m$  match and epitaxy in the two-dimensional layer. On the other hand, if the valence geometry does not fit into these segregated layers structure, one of the layers will be less close-packed and ordered, or the system will not spontaneously form a layered structure. An example of the former situation may be smectic liquid crystals of biphenyl derivatives (Figure 4). There, the biphenyl moieties form a layer, and the tilted alkyl chains form another layer. The mismatch between  $S_m$  of the biphenyl and nontilted alkyl chain

moieties results in the alkyl chain tilt so that the first condition described above is fulfilled (in this case  $n = m = 1$ ). We note that a tilt of  $\sim 30^\circ$  provides excellent ordering and packing for the alkyl chains.<sup>22–24</sup> Recent STM studies clearly show the formation of layered structures of phenyl rings and  $\text{C}_{12}\text{H}_{25}$  chains in didodecylbenzene on highly oriented pyrolytic graphite (HOPG).<sup>13</sup> When the phenyl ring was substituted by three iodine atoms ( $\text{C}_{18}\text{H}_{37}\text{I}_3$ ), its cross-sectional area increased to  $\sim 30$  Å<sup>2</sup>. Here, where  $n = m = 1$ , no tilting mechanism can deal with the cross-section area mismatch, and STM studies indicated the possibility that the alkyl chains interdigitate in the lamellar structure.<sup>25</sup> Clearly, interdigitation of alkyl chains that are normal with respect to the lamella leaves free volume in the layer of the triiodophenyl rings unless these rings tilt by  $\sim 45^\circ$  with respect to the axis normal to the lamella. The STM study suggests that this indeed may be the case.

## Conclusions

In this paper we have developed the concept of *commensurability of intraassembly planes* and discussed its importance in the formation of stable two-dimensional molecular assemblies. We suggest that it is necessary to have commensurability of one good packing arrangement of a layer of one molecular moiety (e.g., tilted alkyl chains) with one good packing arrangement of a layer of another molecular moiety (e.g., herring bone arrangement of straight phenyl rings) to form a match. This, still, is not enough to ensure a spontaneous formation of a two-dimensional solid. It has been shown recently, in the case of van der Waals (vdW) crystals, that layers of different materials can be bonded to each other by vdW forces and that epitaxy is not necessary in all cases.<sup>26–31</sup> This cannot be the case where the intraassembly epitaxy is concerned, since here, valence geometry, i.e., the bond connecting the two intraassembly layers, should have a profound effect on the structure and stability of the final two-dimensional system.

When a match commensurability in cross-sectional areas is accompanied by that of the two-dimensional intraassembly planes, the system should be a two-dimensional solid, provided that valence geometry supports intraassembly match, and entropy effects are not substantial. However, if  $S_m$  match or epitaxy are not perfect, or if the valence geometry does not support intraassembly match, the system may adopt the structure of a smectic liquid crystal (SLC). This may be the case also in a perfect match, when the alkyl chains are too short and entropy effects prevent formation of a solid at room temperature. When the intralayer packing energy is large enough, one can even form stable suspended SLC films.<sup>32</sup> This has been manifested recently in an interesting work where biphen-

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yl and triphenyl systems were found to form such stable suspended SLC films.<sup>33</sup>

It is also important to emphasize that incommensurability of molecular parts does not mean that a two-dimensional assembly cannot be formed. Clearly, two-dimensional assemblies with perfect intraassembly match of atomic planes are in a stable or metastable state of a thermodynamic equilibrium. Such molecular layers in space are close-packed like a normal crystal, exhibiting long-range order. Increasing intraassembly mismatch decreases the cohesive energy and should lead to enhanced defect density, ultimately decreasing the layered structure stability. The stability of the layered assembly can be augmented by chemisorption or physisorption to a solid surface or by applying pressure as is the case on the air-water interface in a Langmuir trough. Thus, even though the unconstrained layered structure is not in a global minimum of the free energy, there are mechanisms of the types mentioned above, that, together with conformational modification,<sup>11</sup> may yield a layered assembly that is in a stable minimum.

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An important conclusion from the ideas discussed in this paper is that alkyl chains may be a dispensable part of a complex molecule when self-assembly (SA) is concerned. Thus, while it is important to have an amphiphilic structure for a good Langmuir-Blodgett (LB) monolayer to be formed, there is a need for an *amphifunctional* molecule for the self-assembly process. (By *amphifunctional* we mean that the molecule should have one part that has a strong affinity—mostly chemical in nature—to the surface under study and another that has a very weak one or none.) This is because in the LB process molecules are organized at the air-water interface, while in the SA process molecules spontaneously organize in a layer structure. Thus, if chemisorption—analogue to the intraassembly valence requirement discussed above—does not disrupt formation of a stable packing arrangement, a good SA monolayer should be formed. Therefore, substituting an alkyl chain on, for example, a planar  $\pi$ -system, may not help, and may even prevent the formation of an ordered layer due to the competition between packing requirements in the sublayers. Hence, it should be possible to form self-assembled monolayers from simple aromatic structures.<sup>34</sup>

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