

Two-Dimensional Phase Behavior of a Bimolecular Porphyrin System at the Solid–Vacuum Interface

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Abstract: The “in vacuo” self-assembly of a two-component porphyrin system on a metal surface is studied by means of scanning tunneling microscopy in the sub-monolayer regime. The observed self-assemblies are systematically analyzed by their dependence on the total coverage and on the ratio of the two components resulting in a two-dimensional phase diagram. In a small region within the parameter space, a mixed surface layer is observed. The results are discussed consistently on the basis of molecule–surface and molecule–molecule interactions as well as thermodynamic aspects, leading to a qualitative comprehension of the phase behavior of the two-dimensional bimolecular system.

1. Introduction

The ability of molecular compounds to self-assemble¹ has been exploited extensively over the past decade to form new materials with unprecedented properties.² Researchers’ comprehension of the mechanisms involved in the formation of self-assembled structures consisting of a single component at atomically clean surfaces has increased enormously in recent years.^{3,4} However, the ability to systematically tailor self-assemblies consisting of more than one component is only slowly evolving, as the principles involved here are more complex and can be co-determined by thermodynamic processes. Instead of forming an intermixed assembly, the evaporation of different molecular compounds onto a surface often leads to a segregation characterized by the formation of domains resem-

bling the single-component⁵ assemblies on the same surface (see ref 6 and the Supporting Information). Only a few examples exist where the formation of an intermixed network consisting of more than one component without specific bonding motifs has been observed, some of which can be found in ref 7. It should be noted that the assembly and intermixing process in the far less studied case at the solid–vacuum interface^{7a,b} significantly differs from that of the solid–liquid assemblies^{7c–g} in that it is restricted to in-plane diffusion due to the significant adsorption strength of the molecular components after adsorption in the vacuum. Thus, our work relates to the thermodynamics of mixed molecular assembly⁸ at the solid–liquid interface, while it aims for understanding and control of the different case at the solid–vacuum interface. Different approaches to ensure intermixing have been investigated, like the use of alkyl chains at the solid–liquid interface,⁹ the accommodation of a second

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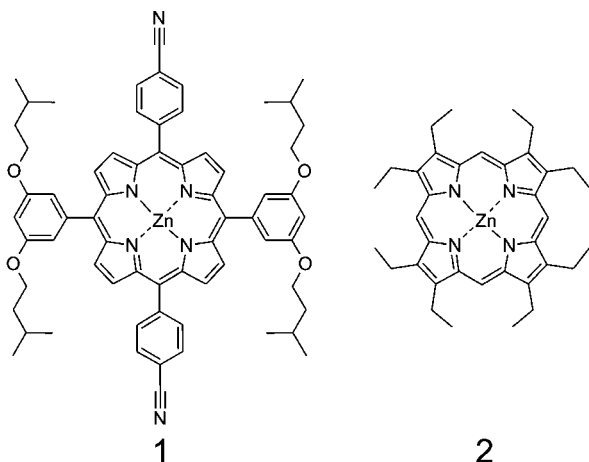


Figure 1. Chemical structures of the Zn(II) porphyrins **1** and **2** used in this study. For details, see ref 4 and the Supporting Information.

component into a pre-existing network,¹⁰ or the use of directional bonding motifs like complementary hydrogen bridges.¹¹ In contrast to the latter, nondirectional bonding motifs are rarely used for bimolecular self-assembly at the solid–vacuum interface, because the assemblies formed are harder to predict as they strongly depend on the delicate molecule–molecule and molecule–substrate interactions influencing the thermodynamic equilibrium.¹² Nevertheless, the use of nondirectional bonding motifs offers a variety of possibilities to control bimolecular self-assemblies, as will be discussed in the following.

In this article we report on the two-dimensional (2D) phase behavior of a bimolecular porphyrin system exhibiting directional and nondirectional bonding motifs on a surface in the vacuum. In a small region in the parameter space at distinct mole fractions and at surface coverages below one monolayer, a highly ordered intermixed network is formed, while across the whole parameter space a large number of different phases have been observed. Figure 1 shows the chemical structures of the two Zn(II) porphyrin derivatives selected for this study. Compound **1** and its single-component self-assemblies, which depend on the surface coverage, are described in detail elsewhere.⁴ The single-component assemblies of **2**, which also depend on the surface coverage, are shown in the Supporting Information (Figure S-2).

2. Experimental Section

All experiments were performed with a commercial Omicron scanning tunneling microscope (STM) under ultra-high-vacuum (UHV, base pressure of 1×10^{-10} mbar) conditions. The STM data were obtained using scanning parameters of about -1.5 V sample bias voltage and 10 pA tunneling current at a sample temperature of 77 K unless indicated otherwise. As a substrate we used an atomically flat Cu(111) single crystal, a representative of a close-packed noble metal surface, which had been freshly cleaned by cycles of sputtering with Ar^+ ions and annealing at 800 K.

Porphyrins **1** and **2** were sublimed from a commercial Knudsen-cell-type evaporator¹³ onto the substrate held at room temperature. This evaporator provided a constant flux of molecules, which was monitored and determined by a quartz crystal microbalance placed close to the sample position.

3. Results

The self-assemblies observed after subsequent evaporation of porphyrins **1** and **2** onto a Cu(111) surface depend strongly on (i) the ratio between the amount of **1** and **2** and (ii) the total number of molecules on the surface. This finding is in concordance with a similar experiment performed at the solid–liquid interface, where the formed assemblies were analyzed as a function of the mole fractions.¹² However, one important difference between the solid–liquid and the solid–vacuum interfaces is the possibility to exchange material by condensation and re-solubilization in thermodynamic equilibrium with the surrounding solution in the first case, which is not possible in the latter case. Thus, in UHV environment, diffusion is strongly hindered at high coverages close to a full monolayer (ML), which can lead to retarded thermodynamic optimization. This makes it convenient to choose the mole-fraction¹⁴ of one component, e.g., x_2 (mole fraction of compound **2**), and the total coverage¹⁵ as parameter space in UHV. In Figure 2a, the diagram containing the experimentally observed phases is shown. The sequence of evaporation does not affect the formation of the assemblies when thermodynamic equilibrium can be reached, i.e., for total coverages below 0.9 ML. This can be related to the fact that, for low coverages, both compounds **1** and **2** are found in a 2D mobile phase at room temperature and the self-assemblies are formed in the subsequent (slow) cooling process. Therefore, also annealing of the sample to temperatures higher than room temperature did not affect the observed self-assemblies. At coverages >0.8 ML, compound **1** is found to form a porous network.⁴ Thus, to consider the effect of the evaporation sequence for high coverages at room temperature, two cases have to be considered.

(i) $x_2 \ll 1$: In this case, the concentration of **1** is high. Thus, when **1** is evaporated before **2**, the porous network of **1** is formed. **2** is found between the networks, indicating that it can diffuse from the network to the copper surface. When **2** is evaporated before **1**, because of the high concentration of **1**, the porous network of **1** is formed and **2** is pushed into the regions between the networks. In this case, the formed assemblies should be independent of the sequence of evaporation, which is consistent with the experimental findings.

(ii) $x_1 \ll 1$. In this case, the concentration of **2** is high. When **1** is evaporated before **2**, **1** is mobile on the surface. The

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(15) In the presented case, the surface coverage can be estimated simply by summing up the single-component coverages.

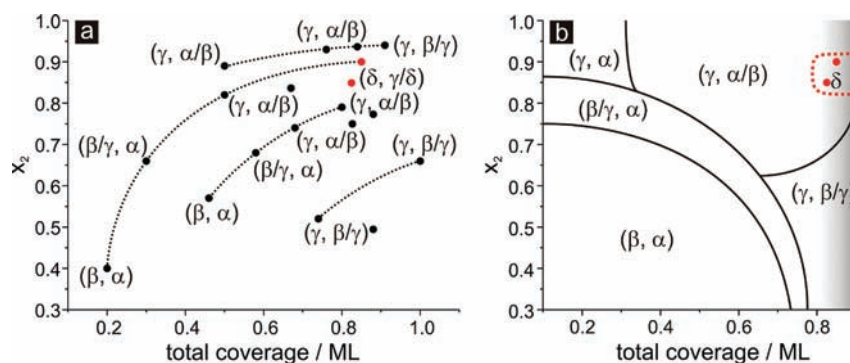


Figure 2. Phase diagrams for the bimolecular system as a function of both mole fraction and total surface coverage. The observed phases are denoted as α (monomers), β (chains), γ (clusters and islands), and δ (mixed network). The first term in the brackets refers to compound **1**, and the second term refers to compound **2**. (a) Experimental data taken from extensive series of single-component and multicomponent assemblies. Each dot represents one experiment; experiments connected by a dashed line have been performed subsequently. (b) Outline of the phase regions in (a) where the same phases are expected. The region where δ can be observed is outlined in red. Note that the transition between the phases is not as sharp as the black lines indicate. The shaded area on the right indicates the region where mass transport is progressively hindered — and thus thermodynamic equilibrium is retarded — due to the increasing total surface coverage and the impossibility to exchange components with the surrounding vacuum.

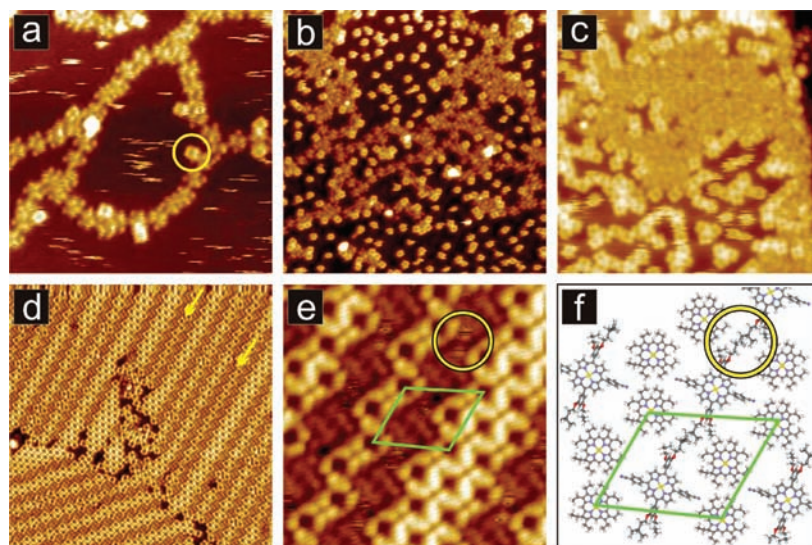


Figure 3. STM images depicting the phase behavior of the bimolecular system of **1** and **2**. The amount of molecules of **1** is kept constant, while the amount of **2** increases from (a) to (d). The phases are denoted as specified in the text: α , monomers; β , chains; γ , clusters and islands; δ , mixed network. For detailed information on the phase behavior, see the main text. (a) STM image taken at 85 K (**1**, 0.15 ML; **2**, 0.05 ML; image size, $25 \times 25 \text{ nm}^2$), noted (β, α) in Figure 2. (b) STM image taken at 77 K (**1**, 0.15 ML; **2**, 0.15 ML; image size, $50 \times 50 \text{ nm}^2$), noted $(\beta/\gamma, \alpha)$ in Figure 2. (c) STM image taken at 77 K (**1**, 0.15 ML; **2**, 0.35 ML; image size, $30 \times 30 \text{ nm}^2$), noted $(\gamma, \alpha/\beta)$ in Figure 2. (d) STM image taken at 77 K (**1**, 0.15 ML; **2**, 0.70 ML; image size, $50 \times 50 \text{ nm}^2$), denoted δ in Figure 2. (e) High-resolution image of the intermixed network δ of **1** and **2** (image size, $10 \times 10 \text{ nm}^2$). Streaks (yellow circle) hint at the location of the alkoxy chains of **1**. (f) Tentative model of the arrangement of the molecules in a fully equilibrated intermixed network δ , which features lines with a perfectly distributed, equal line width. For detailed information, see the main text.

subsequent evaporation of **2** leads to **1** being forced into the porous network of **1**, as shown in Figure 3c. When **2** is evaporated before **1**, stable islands of **2** are formed. The remaining places on the surface left for **1** are few, which is equivalent to **1** being on a very small surface where it can sufficiently diffuse. Thus, the relative concentration of **1** is high, and the porous network is formed. Indeed, this is confirmed by the experimental findings. As a result, also in this case, the observed assemblies are independent of the sequence of evaporation.

From the results presented in Figure 2a, as well as from the single-component phase diagrams (cf. the Supporting Information), we can outline the regions in parameter space where the same phases are expected to be found, as shown in Figure 2b.¹⁶

(16) Note that the transitions between single phases are not as sharp as Figure 2b might imply.

The shaded area indicates regions at high total coverages, where thermodynamic equilibrium is progressively retarded due to hindered mass transport, as mentioned above and discussed below.

To investigate the observed assemblies for the two compounds — α , monomers; β , chains; γ , clusters and islands; and δ , mixed network — we performed several series of experiments in which we evaporated a constant amount of compound **1** onto a Cu(111) surface and then subsequently increased the amount of compound **2** (see the dashed black lines shown in Figure 2a). STM experiments were performed for each of the samples prepared in this series to reveal the characteristics of the observed phase or phases. In the following, we describe one series that leads to a highly ordered mixed network (red spot, phase δ). Starting with a mole fraction of $x_2 = 0.4$ and a total coverage of 0.2 ML (**1**, 0.15 ML; **2**, 0.05 ML), **1** forms the

chain phase known to form at low coverages in the single-component system (phase β_1 , cf. Figures S-2 and S-3 in the Supporting Information), while **2** is mobile on the Cu(111) surface at temperatures above 77 K (phase α). Such mobility is evidenced by “streaky” horizontal lines in the STM images¹⁷ (Figure 3a, taken at 85 K) and might, in principle, be enhanced by the scanning tip, an effect which is not predominant here, as all phases have been observed to form during preparation and were stable irrespective of the duration of our STM investigations. Some molecules of **2** are found attached to the chains of **1** (see, e.g., yellow circle in Figure 3a). In subsequently taken STM images above 77 K, a constant exchange of molecules of **2** is found: molecules in the 2D gas phase condense at the chains while those attached to the chains go into the gas phase again. Below 77 K, molecules of **2** appear quite homogeneously spread (similar to the ones shown in Figure 3b, taken at 77 K).

At a mole fraction of $x_2 = 0.66$ and a total coverage of 0.3 ML (**1**, 0.15 ML; **2**, 0.15 ML), a perturbation of the chains of **1** is observed (Figure 3b): while the chains remain visible, molecules of **1** are also found to cluster, which locally increases the density of **1** on the surface (phase β/γ). Molecules of **2** are found mostly to be isolated and stably adsorbed (phase α).

At a mole fraction of $x_2 = 0.82$ and a total coverage of 0.5 ML (**1**, 0.15 ML; **2**, 0.35 ML), the chains of **1** are no longer observed. Instead, clusters and small areas of the single-component porous network of **1** are found (phase γ , Figure 3c). Interestingly, when **1** is evaporated as the sole component onto a Cu(111) surface, this network is only observed at coverages >0.7 – 0.8 ML.⁴ Molecules of **2** are found either attached to the borders of the structures of **1** (phase α) or in a chain-like arrangement (phase β) when no molecules of **1** are nearby (Figure 3c). This arrangement resembles the single-component assembly of **2** at low sub-monolayer coverages.

At a mole fraction of $x_2 = 0.90$ and a total coverage of 0.85 ML (**1**, 0.15 ML; **2**, 0.70 ML), the formation of an intermixed network is observed (phase δ , Figure 3d). It consists of alternating rows of the two components, with the rows formed by **2** exhibiting a higher contrast in STM images. Due to the excess of **2**, single-component networks of **2** are also found. This phenomenon is well known in the bulk, where a near-field ordering can be observed in close vicinity to the optimal parameters required for the formation of a mixed phase accompanied by a segregation of the excess component.¹⁸ However, in our case no regular intermixing was observed for an excess of compound **1**. Also, the near-field ordering is not perfect: The rows formed by **2** differ in their width, while the rows of **1** always exhibit the same width (cf. ref 19). This width fluctuation is considerable in all our data showing the mixed phase. The formation of an ideal network in which also the rows of **2** exhibit an equal, minimal width (such as the rows marked with an arrow in Figure 3d) by thermodynamic equilibration is retarded at the high surface coverage, which hinders the diffusion and mass transport of the molecules required to form

Table 1. Densities of the Single-Component Networks of **1** and **2** as Well as for the Fully Equilibrated Intermixed Network, As Derived from STM Data

compound	density/molecules per nm ²
1 (coverage >0.8 ML)	0.30 ± 0.02
2 (islands)	0.60 ± 0.01
1+2 (fully equilibrated network)	0.44 ± 0.02

a fully equilibrated phase. Thus, annealing to a temperature slightly higher than 77 K and slow re-condensation by carefully lowering the temperature again should better equilibrate the intermixed phase. Note that this width fluctuation is not in contrast with the intermixed network being a thermodynamically stable phase.

Figure 3f shows a model of the fully equilibrated intermixed network. Its unit cell (green rectangle) consists of one molecule of **1** and two molecules of **2**, thereby depicting that the ratio for the fully equilibrated intermixed network is $N_1:N_2 = 1:2$. Two main contributions can be identified for the intermolecular interactions inside the unit cell. First, the cyano groups of **1** can most probably interact via weak hydrogen-bond-like contacts with the ethyl chains of adjacent molecules of **2**, as these chains are likely immobile at the investigated temperatures. Second, the alkoxy chains of **1** can not only interact via van der Waals (vdW) interactions with the alkoxy chains of adjacent molecules of **1**, but also with the ethyl chains of adjacent molecules of **2**. Interestingly, the antiparallel CN \cdots CN dipole motif observed in the chains of **1** (see ref 4) is not found anymore. Furthermore, the alkoxy chains of **1** are, in contrast to the ethyl chains of **2**, not completely immobilized, as streaks in the STM images prove (Figure 3e, yellow circle). This might be attributed to the facts that (i) branching of the alkoxy chains weakens the vdW interaction with another alkoxy chain of the same kind as they cannot lie parallel, which is needed for optimal vdW interactions, and (ii) The alkoxy chains are longer than the ethyl chains and thus exhibit a higher conformational entropy than the latter.²⁰ We are currently investigating the influence of different alkoxy chain substituents on the 2D intermixing phase behavior of porphyrins. This work aims at improved control of bimolecular assemblies by directional and non-directional bonding motifs.

4. Discussion

From the microscopic point of view, the relative interaction forces as established in surface science have to be discussed to explain the behavior of the investigated bimolecular system. Specifically, this involves (i) the interactions between each of the molecular compounds and the metallic surface, (ii) the interactions between components of the same kind, and (iii) the interactions between different components.

Table 1 shows the densities of the 2D periodic single-component assemblies observed for porphyrins **1** and **2** on the Cu(111) surface as well as the density of the fully equilibrated intermixed network (Figure 3f). As can be seen, the density of the fully equilibrated intermixed network d_{1+2} (0.44 molecules per nm²) is smaller than the density calculated from the single-component networks for a 2:1 mixture $(N_1d_1 + N_2d_2)/(N_1 + N_2) = 0.5$ molecule per nm². Thus, a full monolayer of the mixed

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network would contain less molecules than a corresponding monolayer consisting of single-component networks with N_1 molecules of **1** and N_2 molecules of **2**, which leads to a lower adsorption energy per surface area. This indicates that the mixing process is not induced by the molecule–surface interactions only.

We now estimate the intermolecular interaction energies which, unlike the case presented in ref 12, are not known for the compounds used in this study. Estimating the intermolecular interactions is not straightforward, mainly because the type and magnitude of intermolecular interaction for **1** depends on the surface coverage. In a recent publication,⁴ we have shown that the alkoxy chains have to be condensed first, e.g., by increasing the molecular packing density, in order to effectively undergo vdW interactions. Nevertheless, some conclusions on the intermolecular interactions can be drawn from STM images:

(i) As already stated above, for low partial coverages of **2** ($x_2 \ll 1$) in coexistence with **1** and low total coverages, the two different compounds can interact efficiently via vdW forces acting between their side groups, as a partial fraction of **2** adheres to the chains of **1** (Figure 3a). Strictly speaking, the interactions U_{12} between **1** and **2** must be considerably stronger than the interactions U_{22} between **2** and **2**, as no clusters of **2** were observed at corresponding coverages (cf. Figure 3b). Furthermore, the condensation of **2** at the chains of **1** is especially interesting, because neither **1** nor **2** interacts efficiently with itself via vdW forces at low total coverages. Only when the partial coverages are increased, **2** condenses into clusters and islands. In the first case, we assign this behavior to the entropic motion of the alkoxy chains of **1**, which hinders efficient interactions via vdW forces at low partial coverages.⁴ In the second case, an interesting analogy to the phase behavior of a real gas in 3D can be seen: The density of molecules per area, i.e., the coverage in the 2D gas phase, is — in analogy to the molecules per volume in a 3D gas — a measure for the pressure. On the surface, as in 3D systems, an increase of pressure/coverage may lead to a condensation of molecules. This is also observed for **2** at increasing coverages (see Figure 3b,c as well as Figures S-2 and S-3 in the Supporting Information).

(ii) Compound **1** is observed to participate in different bonding motifs at different coverages. At low coverages, **1** is able to form chains via cyano-induced dipole–dipole interactions. At higher coverages, the intermolecular alkoxy–alkoxy interaction of **1** via vdW forces becomes more effective.⁴ Thus, the interaction U_{11} is strongly coverage dependent. Nevertheless, the STM images implicate that $U_{11} > U_{12}$ for all coverages. This explains why no intermixing is observed for an excess of component **1** ($x_1 > x_2$): The strong intermolecular forces between **1** effectively hinder the formation of an interaction between **1** and **2**. We speculate that only the presence of **2** in a sufficient amount compared to **1** prevents **1** from forming a single-component assembly. This enables us to identify a first condition for intermixing: $x_2 \gg x_1$. In other words, one has to dilute **1** in **2**. This hypothesis is also supported by the fact that, within the mixed network, **1** interacts with **1** via a bonding motif not found in the single-component assemblies. This indicates that the single-component bonding motif between **1** and **1** is effectively hindered by the interaction with **2** in the mixed network. The interactions between **2** and **2**, in contrast to those between **1** and **1** as described above, are vdW based for all coverages. However, only at high total coverages this

component can interact efficiently via vdW forces with itself, as described above, which is apparently also a necessity for the formation of the mixed network. Thus, **2** not only needs to have a high partial coverage (condition 1, $x_2 \gg x_1$), but also a high total coverage is needed (condition 2) for the formation of the mixed network. This explains the position of δ in the phase diagram. As known from bulk materials, one criterion necessary for intermixing is $(U_{11} + U_{22}) < 2U_{12}$.²¹ Thus, intermixing is possible even if $U_{11} > U_{12}$ when $U_{22} \ll U_{11}$. However, as stated above, at coverages close to a full monolayer, diffusion and mass transport of the molecules is retarded, which prevents the formation of an intermixed network at very high coverages of nearly a full monolayer (condition 3). In short, we have identified three conditions that explain the position of the intermixed phase δ in the phase diagram.

The phenomenon that thermodynamically influenced mixtures can form regular intermixed phases at distinct mole fractions is well known in the 3D bulk and in liquid.²² It can be understood by the interplay of the entropy of the system, including the *entropy of mixing*, which has no counterpart in single-component systems, and the *total enthalpy*, which represents the interaction forces as described above. This interplay is accounted for by the *free energy* F of the system. For an ordered mixing to occur, F as a function of the mole fraction x needs to have a minimum. Only in the vicinity of the minimum can regular intermixing occur. This is in analogy to the observation that a thermodynamically stable intermixed network is formed only for distinct mole fractions.

A striking difference, however, between classical thermodynamic systems in liquid or in the bulk and the 2D system described herein is the strong influence of the total amount of molecules, via the intermolecular spacing, on the mixing process in the monolayer. We have shown that the surface coverage next to other parameters can influence (i) the type of bonds occurring,²³ (ii) the entropy/enthalpy balance in the case of flexible substituents, and (iii) the diffusive mass transport on the surface. This complicates the prediction of whether and how mixing between two or more components will occur on the surface.

5. Summary and Conclusions

Our detailed study on the bimolecular porphyrin system demonstrates the main mechanisms influencing the thermodynamics and the phase behavior/self-assembly of a multicomponent system at the solid–vacuum interface. We have shown that directional bonding motifs, specifically the CN \cdots CN and the CN \cdots H, can be complemented by nondirectional bonding motifs, here the entropic alkane mobility/condensation. We have also shown that such motifs, in combination, are suitable for tailoring supramolecular bimolecular layers. We have conveyed a type of analysis already performed for the solid–liquid interface (refs 7c–f) to the solid–vacuum interface and also identified the limits of this approach (i.e., the hindered mass

(21) Dill, K. A.; Bromberg, S. *Molecular Driving Forces: Statistical Thermodynamics in Chemistry & Biology*; Garland Science: Oxford, 2002.

(22) A complete discussion of the thermodynamic evolution of surface layers undergoing self-assembly goes beyond the scope of this work, and the basic equations are described in many textbooks, e.g., in ref 18. More detailed calculations are currently in progress.

(23) Wang, L.; Qi, D. C.; Liu, L.; Chen, S.; Gao, X. Y.; Wee, A. T. S. *J. Phys. Chem. C* **2007**, *111*, 3454.

transport in 2D at high coverages). We want to stress that, due to the missing desorption/readsorption thermodynamics at the solid–vacuum interface, the hindered mass transport at high coverages has to be carefully considered when tailoring intermixed layers.

Using STM, detailed microscopic insight into the 2D phase behavior of such a bimolecular system is gained. Its behavior is consistently discussed in terms of the complex molecule–surface and molecule–molecule interactions of the molecules with their specific architecture bearing different substituents. We have given an estimation of the phase-diagram for the bimolecular system dependent on both the mole fraction and the total amount of molecules, taking into account that, at the solid–vacuum interface, diffusive mass transport is always hindered at coverages close to full monolayers. Our analysis goes beyond established analytical methods for multicomponent systems at the solid–vacuum interface, narrows the gap to the solid–liquid interface, and also enhances knowledge in crystal engineering of surface-bound layers.

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Supporting Information Available: Results on a 2D bimolecular porphyrin system exhibiting only segregation; determination of the mole fraction; Figure S-1, chemical structures of **1** and **2**, as well as **3**, which is used in the different set of experiments presented herein; Figure S-2, STM images of the single-component phases of **1** and **2** on a Cu(111) surface; Figure S-3, phase diagram for the single-component phases of **1** and **2** as a function of the coverage; Figure S-4, STM images of the bimolecular system of **1** and **3**; and Figure S-5, STM images of **3** found as substitutional defects in the chains of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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