How Equilibrium Gets Mimicked During Kinetic and Thermodynamic Control in Porphyrin and Phthalocyanine Self-Assembled Monolayers

Jeffrey R. Reimers

International Centre for Quantum and Molecular Structures and School of Physics, Shanghai University, Shanghai 200444 China

School of Mathematical and Physical Sciences, University of Technology Sydney, Sydney, NSW 2008 Australia

Abstract. The recent review of Hipps and Mazur is extended to consider the origins and significance of their conclusion that “surface structures [may] vary with relative component concentration in a way that may mimic equilibria but is not”. How this situation can arise during self-assembly is discussed, as well as a range of qualitative and quantitative observations and high-level free-energy calculations that document the effect for *meso*-tetraalkylporphyrins self-assembled monolayer polymorphs. This leads to discussion of modern challenges facing quantification of the effects caused by kinetic control, as well as to the usefulness of equilibrium mimicking in the design and synthesis of self-assembled monolayers.

In “Kinetic and Thermodynamic Control in Porphyrin and Phthalocyanine Self-Assembled Monolayers”, Hipps and Mazur summarize a wide range of evidence indicating that porphyrin and phthalocyanine self-assembled monolayers on graphite and gold are controlled by kinetic effects and are not in thermal equilibrium.[1] This understanding is critical to research spanning many proposed applications of these systems and is likely to be widely descriptive of many other systems of current interest. An important conclusion drawn is that “surface structures vary with relative component concentration in a way that may mimic equilibria but is not”. However, the review article does not elaborate on how surface structures vary with concentration, how this mimicking effect arises, its practical consequences for device design, and important future research directions required to understand it.

Focus on these wider issues associated with kinetic control of self-assembled monolayer (SAM) structure has recently been drawn through a combined experimental and *a priori* computational study of the free energy of polymorphism of *meso*-tetraalkylporphyrins.[2] This involved examination of the dependence of the free energy on chain length and porphyrin metallo substitution[3] and embodies key results from earlier studies.[4-9] When the alkyl chain length exceeds 10, SAMs are observed in scanning tunneling microscopy (STM) images of these molecules on highly-ordered pyrolytic graphite (HOPG) surfaces at interfaces with organic solvents such as 1-phenyloctane, *n*-tetradecane, and octanoic acid. However, these SAMs can display polymorphism, with different regions of the SAM having different adsorbate coverages. Also, as the alkyl-chain length changes, polymorphs of about the same density can take on very different SAM lattices and present very different STM-image structures within each cell.

Critical to the understanding of those results is that a SAM, once formed, does not respond to external perturbations in the way expected if the observed polymorphism reflected domains in chemical equilibrium with each other.[8] This is the issue elaborated on in detail in the review of Hipps and Mazur.[1] Another critical issue is that the observed relative concentrations of the different polymorphs respond to changes in SAM formation conditions as if some type of equilibrium existed, alluded to in the review as “mimicking equilibrium”. Changes in the initial conditions are widely observed to lead to differing polymorph ratios, with crude techniques developed for measuring these ratios and converting this data into *apparent* polymorph free-energy differences.[2-3]

Hipps and Mazur cast the discussion of kinetic versus thermodynamic control in terms of three characterizing questions:

1) Are tectons [adsorbed molecules] exchanging between surface and solution?

2) Is the system at steady state?

3) Is the state of the system independent of history? That is, does a change in system concentration or temperature result in the same state as when the sample is initially prepared with those parameters?

However, there is also a fourth question of great significance when it comes to understanding polymorphic SAM structures initially formed from a single chemical environment:

4) Is the relative concentration of polymorphic domains in SAMs formed without external perturbation different from expectations based on inter-domain equilibrium?

While Question (1) focuses on equilibrium between the solution and SAM and Questions (2) and (3) focus on what happens either spontaneously or in response to external perturbation after initial formation, Question (4) focuses on equilibrium between polymorphic domains within an initially prepared SAM. If the answer to *any* of these four questions is “yes”, then the SAM is under kinetic control rather than thermodynamic control, with the system not being describable using equilibrium distributions. However, the same answer is not required for all four questions, with differing answers revealing fundamentally important information concerning the chemistry of self assembly.

Figure 5 from the review of Hipps and Mazur cartoons the potential-energy landscape for a molecule moving from solution into a SAM,[1] with resulting discussion concluding that entropy is critical to SAM formation. Critical aspects of their profile concerning polymorphism are represented in Fig. 1, modified to include entropy to make a free-energy landscape. To understand such a cartoon, one must recognize that the aspect of the free energy profile that is most pertinent to understanding SAM growth can change in nature depending on the stage of growth and the chemical process of interest. If a structure is regarded as essentially fixed, except for some single-molecule reaction such as the addition or removal of a molecule to/from the SAM or the reorientation of the molecule within the SAM, then the free energy per molecule is most relevant. However, when considering equilibrium between large SAM domains, the free energy per unit surface area in each domain becomes the critical quantity. The free energy of relevance is always the one that encompasses all chemical changes embodied in the process of interest. In the early stages of SAM growth, small clusters of molecules must appear on the surface. Such clusters have not been the subject of intense research as they are dynamic on time scales shorter than that required to capture STM images, consequently demanding other approaches to characterization. Only when SAMs remain stable on the timescale of STM measurements (of order of tens of seconds) can images be recorded. The domain sizes of ordered regions seen in these images can be small (of order 10 molecules), are often of order 10^3 molecules, can be large with 10^6 molecules, and much more.

Figure 1 shows the simplest-possible model capturing this chemistry, which depicts the conversion of solvated molecules to some conceived intermediate cluster to the dynamic SAM observed by STM. The double-well potentials shown in blue represent unimolecular interconversion of two intermediate clusters depicting different polymorphs, while those shown in purple depict this process in the final SAM. Unimolecular processes involve only the internal rearrangement of an existing surface-bound structure, rather than loss or gain of molecules to/from solution. Sequential unimolecular processes occurring at domain interfaces can convert one polymorph to another. Alternatively, the red curves depict molecule adsorption/desorption processes that change domain size: processes which convert the original solvated molecule and surface to the bound clusters and then to the final SAM domains. These processes could also be involved in equilibration of formed SAM domains with each other.

A significant feature is that the free energies of the species involved, as well as the depicted activation free energies, are both domain size and polymorph dependent. Molecules interact with each other via both short-range and long-range forces; it is much more difficult to rearrange a molecule when it is tightly integrated with many neighbors than when loosely connected. The process of lowest free-energy available to any particular cluster/polymorph/interface is always the one of greatest interest.

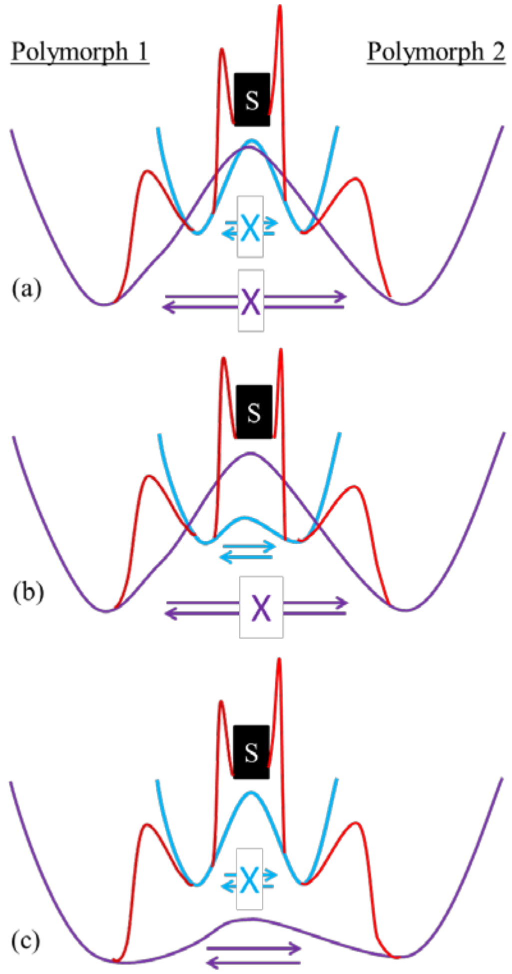

Figure 1. Cartoon of processes involved in SAM formation, sketching free energy as a function of characteristic nuclear coordinates. Different colors show free-energy surfaces as functions of different coordinates depicting processes appropriate to different stages of SAM formation: blue represents unimolecular processes in small surface-bound clusters present on timescales much shorter than can be observed by STM, purple represents unimolecular processes in polymorph domains detectable by STM, and red curves show paths for SAM growth/destruction. "S" represents the free energy of an adsorbate molecule in solution and a solvated surface, while the left-side and right-side local minima depict properties of two polymorphic forms of the SAM. Arrows indicate functioning equilibrium processes, or "X", the lack thereof.

Three characteristic scenarios are depicted in the figure. In (a), the activation free energies for processes involving the two polymorphs are quite different, leading to differing rate constants for formation processes. Polymorph 1 has a much lower barrier for initial SAM formation, consequently the final SAM is expected to be dominated by this polymorph, despite the similarity of the final free energies of the two polymorphs. The produced SAM is kinetically trapped on the time scale of the experiments as the barriers for both unimolecular and dissociative equilibration are too high. The answers to Questions (1)-(4) all indicate that this system is kinetically trapped.

Alternatively in (b), a scenario is depicted in which all rate constants for processes involving SAM formation are similar for both polymorphs. As before, the barriers for both unimolecular equilibration between SAM polymorphs and dissociative/associative equilibration between SAM and solution are too high, which makes the final SAMs kinetically trapped, with answers of "yes" to questions (1)-(3). However, the analogous barriers for small clusters appearing at the early stages of SAM formation will in general be different from those depicting the final SAM components, being typically much less owing to reduced intramolecular coordination. If the barrier for either unimolecular or dissociative equilibration for the intermediate clusters is sufficiently small, equilibrium will be established between these transient species. In this case, Question (4) will yield an answer of "most likely no".

A feature of Figs. 1a and 1b is that the barriers for conversion of one SAM polymorph to the other, by intramolecular rearrangement of the molecules at the interface between the polymorph domains, is taken to be large, preventing equilibration. However, in (c), this barrier is reduced to indicate a scenario in which SAM polymorphs are in equilibrium with each other, but not in equilibrium with the molecules in solution. As in (b), Question (4) will in this case also yield an answer of "most likely no".

Scenarios (b) and (c) result in answers to Question (4) that are inconsistent with the answers to Questions (1)-(3), because an equilibrium distribution of product polymorphs is a *required* but not a *sufficient* condition for demonstrating a system in equilibrium. These are the types of scenario referred to by Hipps and Mazur as "mimicking equilibrium". In (c), the polymorph-domain equilibration process could be observed by STM, whereas in (b), equilibrium apparent to measurements made on time scales shorter than those currently accessible determine the relative composition of polymorph domains in the final SAM, despite the final SAM being kinetically trapped.

The widely applied procedure in STM imaging, of varying all initial conditions until an interesting imageable SAM is produced, works because SAMs often respond to changes in initial conditions in qualitatively foreseeable ways through answers of "apparently no" to Question 4. Indeed, this qualitative understanding led to the naïve notion that SAMs of porphyrins, phthalocyanines, and many other systems are in thermal equilibrium. The papers reviewed by Hipps and Mazur are very important in that they show this to be not always true, with kinetic control being a critical aspect of porphyrin and phthalocyanine SAMs. Hence their key conclusion is : "surface structures vary with relative component concentration in a way that may mimic equilibria but is not".

Going further, simplistic ideas concerning equilibrium can qualitatively describe aspects of prepared SAMs crucial to SAM development and deployment is a critical feature demanding understanding that presents important current challenges. What is needed are methods for quantifying the overall kinetics scheme, including parameters describing the equilibrium and kinetics scenario depicted from the potential-energy surfaces sketched in Fig. 1.

Much data pertinent to understanding kinetic versus thermodynamic control is summarized by Hipps and Mazur.[1] A significant system discussed is *meso*-tetraalkylporphyrin SAMS on HOPG formed from organic solution, and henceforth we consider properties of this chemical class.

Recent data analysis techniques have shown that quantification of the polymorphs found in *meso*-tetraalkylporphyrin SAMs is possible,[2-3] leading to experimental estimates of what SAM polymorph-component free energies would be provided that they were in thermal equilibrium. Such data is the starting point for quantitative analysis of the effects of kinetic control, but it is difficult to obtain an accurate evaluation as one must be sure to have averaged over large enough image sizes to represent properly a macroscopic SAM. Also in SAMs of interest, the appearance of a significant fraction of the adsorbed molecules near domain boundaries, as well as the presence of possibly large structurally unresolved domains, often complicates analysis. Clearly much better techniques for measuring apparent free-energy differences are required. While some quantitative data is available for the dependence of apparent equilibrium constants on initial conditions,[2-3] greatly improved data is required to quantify just how deviations from simple equilibria become manifest. From the understanding of these differences will flow quantification of the kinetics schemes mooted by Fig. 1.

Another way to address the issues raised is through computer simulations of the free energies depicting equilibration and kinetic processes. Simulations have been performed for *meso*-tetraalkylporphyrin SAMs, investigating the most basic question as to whether or not polymorph proportions in SAMs reflect calculated equilibrium free-energy differences.[2-3] Historically, molecular mechanics methods based on empirical force fields have been applied in applications of this type for other chemical systems and shown to be useful.[10-14] Questions always remain concerning the quality of the empirical force fields used, however, and an alternate approach is to use *a priori* computational methods based on, say, density-functional theory (DFT). Only recently have quantitatively reliable DFT methods been developed for treating the van der Waals attraction critical to applications such as porphyrin adsorption,[15] with approaches appropriate for wide-ranging chemical scenarios involving strong van der Waals forces reviewed.[16] When a variety of methods were applied to calculate polymorph free-energy differences for *meso*-tetraalkylporphyrin SAMs on HOPG below organic solvents, computational methods, recognised as being of the highest quality available, were found to give very similar results, independent of approach and method type.[2-3, 15, 17] Hence one would expect these *a priori* simulations to provide the correct semi-quantitative description of the free-energy relationships underpinning polymorphism.

The key issue then becomes how the quantitative *a priori* predictions for polymorphism free energies of *periodic* SAMs compare to those deduced experimentally concerning the energies of either *periodic* SAM polymorphs (if Fig. 1c applies) or *intermediate* structures (if Fig. 1b applies). Results revealed a very strong correlation, with the computed equilibrium free energies predicting which polymorphs were observed as a function of alkane chain length.[10-14] Tens of thousands of possible polymorphs were considered, but only 40 of these fulfilled essential qualitative criteria, with optimization of these 40 leading to 22 stable polymorphs depicting the observed medium-density phases of the *meso*-tetraalkylporphyrin SAMs. To within an error of just 1 kcal mol^{-1}, these simulations were able to predict the observed polymorphs.

That such predictions can be made is a feature supported by the kinetics schemes presented in Fig. 1b and Fig. 1c. If the SAM polymorphs can come to equilibrium without major exchange of molecules with the solvent (Fig. 1c), then some equilibrium process remain operative in the final SAM. If this does not occur, even still the kinetics parameters controlling the rates of domain growth and decay at all stages of the SAM formation process would be expected to vary only slightly with alkane chain length, leaving the equilibrium depicted between the intermediary structures as the primary controller of the final SAM composition (Fig. 1b). By either mechanism, a kinetically trapped SAM gets its composition determined by an intermediary equilibration process, explaining how it is that kinetically trapped SAMs can "mimic equilibrium".

Other critical data concerning *meso*-tetraalkylporphyrin SAM formation also flows from Fig. 1. These SAMs are only observed when the alkyl chain length exceeds 10, an effect that previously was naively attributed to the attraction between HOPG and adsorbate molecules becoming too small at short chain lengths. The calculations, however, suggest a different scenario. Free-energy differences rather than molecule-surface attraction controls binding, with these differences predicted to be small values (order 10 kcal mol^{-1}) arising as a result of cancellation of strong molecule-surface attraction (100-400 kcal^{-1} depending on chain length) nearly completely opposed by combined solvation and entropy contributions.[2] The near-cancellation of three large contributions to the free-energy means that all of them are critically important to SAM formation, with small variations in any one possibly exerting a controlling influence. However, rather than becoming weaker as the chain length decreases, the total free-energy changes were predicted to enhance, naively favoring SAM formation.[3] The critical feature revealed by the calculations is that the number of polymorphs with nearly equal free energies increases dramatically as the chain length decreases. This means that the lack of observation of SAMs for short-chained molecules is a *kinetic effect* involving the interplay of many species, with the SAMs being trapped in a dynamic form not conducive to STM imaging.[3]

Already mentioned is the need for improved experimental techniques to measure polymorph concentrations and hence determine the free-energy differences that would characterize a SAM if it were in equilibrium. Coupled with this is the need to develop improved computational methods for SAM structure prediction and free energy calculation, also techniques for dealing with aperiodic intermediary structures. Going further, computational methods need also be developed to evaluate the transition-state free-energies depicted in Fig. 1. This is a more difficult task, as first those transition states would need to be determined and characterized. This approach leads to an intrinsic shortcoming of the figure- it characterizes the self-assembly process in a minimalist way involving just a *single* intervening state with its characteristic time scales for production, equilibration and destruction, yet in reality a *continuum* of such states exists with a *continuum* of associated time scales. Hence a much clearer physical picture is required if simulations are to provide chemical insight rather than just predict some observed property. Real progress thus requires new experimental techniques that can work on timescales much shorter than STM experiments so that understanding of SAM formation can be obtained on the ps, ns, μs, and ms timescales, experiments that can detail all chemical processes leading to the production of the final SAM.

.

Funding Sources

I thank the Chinese National Science Foundation for support through grant 1167040630.

REFERENCES

.

1. Hipps, K. W.; Mazur, U., Kinetic and Thermodynamic Control in Porphyrin and Phthalocyanine Self-Assembled Monolayers. *Langmuir* **2017,** *10.1021/acs.langmuir.7b02672.*
2. Reimers, J. R.; Panduwinata, D.; Visser, J.; Chin, Y.; Tang, C.; Goerigk, L.; Ford, M. J.; Sintic, M.; Sum, T.-J.; Coenen, M. J. J.; Hendriksen, B. L. M.; Elemans, J. A. A. W.; Hush, N. S.; Crossley, M. J., A priori calculations of the free energy of formation from solution of polymorphic self-assembled monolayers. *Proc. Natl. Acad. Sci. U.S.A.* **2015,** *112* (45), E6101-E6110.
3. Reimers, J. R.; Panduwinata, D.; Visser, J.; Chin, Y.; Tang, C.; Goerigk, L.; Ford, M. J.; Sintic, M.; Sum, T. J.; Coenen, M. J. J.; Hendriksen, B. L. M.; Elemans, J. A. A. W.; Hush, N. S.; Crossley, M. J., From chaos to Order: Chain-Length Dependence of the Free Energy of Formation of Tetraalkylporphyrin Self-Assembled Monolayer Polymorphs *J. Phys. Chem. C* **2016,** *120* (3), 1739-1748.
4. Hulsken, B.; Van Hameren, R.; Thordarson, P.; Gerritsen, J. W.; Nolte, R. J. M.; Rowan, A. E.; Crossley, M. J.; Elemans, J. A. A. W.; Speller, S., Scanning tunneling microscopy and spectroscopy studies of porphyrins at solid-liquid interfaces. *Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers* **2006,** *45* (3 B), 1953-1955.
5. Katsonis, N.; Vicario, J.; Kudernac, T.; Visser, J.; Pollard, M. M.; Feringa, B. L., Self-Organized Monolayer of meso-Tetradodecylporphyrin Coordinated to Au(111). *J. Am. Chem. Soc.* **2006,** *128* (48), 15537-15541.
6. Visser, J.; Katsonis, N.; Vicario, J.; Feringa, B. L., Two-Dimensional Molecular Patterning by Surface-Enhanced Zn-Porphyrin Coordination. *Langmuir* **2009,** *25* (10), 5980-5985.
7. Chin, Y.; Panduwinata, D.; Sintic, M.; Sum, T. J.; Hush, N. S.; Crossley, M. J.; Reimers, J. R., Atomic-Resolution Kinked Structure of an Alkylporphyrin on Highly Ordered Pyrolytic Graphite. *J. Phys. Chem. Lett.* **2011,** *2* (2), 62-66.
8. Coenen, M. J. J.; Cremers, M.; Boer, D. d.; Bruele, F. J. v. d.; Khoury, T.; Sintic, M.; Crossley, M. J.; Enckevort, W. J. P. v.; Hendriksen, B. L. M.; Elemans, J. A. A. W.; Speller, S., Little exchange at the liquid/solid interface: defect-mediated equilibration of physisorbed porphyrin monolayers. *Chem. Commun.* **2011,** *47*, 9666–9668.
9. Coenen, M. J. J.; den Boer, D.; van den Bruele, F. J.; Habets, T.; Timmers, K. A. A. M.; van der Maas, M.; Khoury, T.; Panduwinata, D.; Crossley, M. J.; Reimers, J. R.; van Enckevort, W. J. P.; Hendriksen, B. L. M.; Elemans, J. A. A. W.; Speller, S., Polymorphism in porphyrin monolayers: the relation between adsorption configuration and molecular conformation. *Phys. Chem. Chem. Phys.* **2013,** *15* (30), 12451-12458.
10. Blunt, M. O.; Adisoejoso, J.; Tahara, K.; Katayama, K.; Van der Auweraer, M.; Tobe, Y.; De Feyter, S., Temperature-Induced Structural Phase Transitions in a Two-Dimensional Self-Assembled Network. *J. Am. Chem. Soc.* **2013,** *135* (32), 12068-12075.
11. Killian, B. J.; Kravitz, J. Y.; Gilson, M. K., Extraction of configurational entropy from molecular simulations via an expansion approximation. *J. Chem. Phys.* **2007,** *127* (2), 024107.
12. Hensen, U.; Lange, O. F.; Grubmueller, H., Estimating Absolute Configurational Entropies of Macromolecules: The Minimally Coupled Subspace Approach. *Plos One* **2010,** *5* (2), e9179/1-8.
13. Künzel, D.; Groß, A., Influence of the solvent on the stability of bis(terpyridine) structures on graphite. *Beilstein Journal of Nanotechnology* **2013,** *4*, 269-277.

14. Meier, C.; Roos, M.; Künzel, D.; Breitruck, A.; Hoster, H. E.; Landfester, K.; Gross, A.; Behm, R. J.; Ziener, U., Concentration and Coverage Dependent Adlayer Structures: From Two-Dimensional Networks to Rotation in a Bearing. *J. Phys. Chem. C* **2010,** *114* (2), 1268-1277.

15. Reimers, J. R.; Li, M.; Wan, D.; Gould, T.; Ford, M. J., Surface adhesion. In *Noncovalent interactions in quantum chemistry and physics: Theory and applications*, Otero de la Roza, A.; DiLabio, G., Eds. Elsevier: Amsterdam, 2017; p Ch. 13.

16. Reimers, J. R.; Ford, M. J.; Marcuccio, S. M.; Ulstrup, J.; Hush, N. S., When van der Waals and chemical forces compete: gold-sulfur surfaces and nanoparticles. *Nature Rev. Chem.* **2017,** *1* (2), 0017.

17. Reimers, J. R.; Ford, M. J.; Goerigk, L., Problems, successes and challenges for the application of dispersion-corrected density-functional theory combined with dispersion-based implicit solvent models to large-scale hydrophobic self-assembly and polymorphism. *Mol. Simul.* **2015,** *42* (6-7), 494-510.

TOC Graphic