

# Steering Surface Reactions with Molecular Assembly Strategy

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Controlling molecular adsorption and assembly at surface is one of the major challenges in surface chemistry. While molecular adsorption is dictated by molecule-substrate interaction, molecular assembly is primarily balanced by weak inter-molecule and molecule-substrate interactions under vacuum conditions. Therefore, a slight change in the building block structure or an input of small external energy could drastically shift the balance and hence the assembling structures at surface as well. This is relating to developing new methodologies for molecular self-assemblies at surfaces. Generally, people have been adopting two strategies to tackle surface reaction kinetics: changing reaction temperature (*i.e.*,  $T$  in thermal chemistry) or reaction energy barrier (*i.e.*,  $E_a$  in catalysis), according to the Arrhenius equation which describes the reaction rate constant by  $k=A\exp(-E_a/RT)$  with  $T$  and  $E_a$  in the exponential term. However, people pay less attention to the pre-exponential factor,  $A$ , which relates to ordering, environment and the like of the reacting molecules. Employment of the molecular assembly strategy to tweak the surface reaction rate constant by fine-tuning molecular docking patterns, restricting molecular adsorption sites, tweaking local molecular collision, reaction probability and the like is actually relating to functionalities of molecular self-assembly. Such an approach would bring the molecular assembly strategy into a new horizon with real applications in surface chemistry.

In terms of its applicability, the molecular self-assembly approach can be made use of as a new strategy to steer on-surface reactions in two main manners: assembly-assisted and assembly-involved reactions. The main effects of the self-assembly strategy are threefold: tweaking reaction selectivity, changing reaction pathway and restricting reaction site. The governing principle behind is that the assembly strategy can invoke a surface confinement effect that affects the energy barrier and pre-exponential factor in the Arrhenius equation for the dynamics of the target reaction. In this presentation, I'll talk about several case studies to demonstrate how to employ the molecular self-assembly strategy to steer surface reactions, in particular on the aspects mentioned above. As a matter of fact, the molecular self-assembly strategy can also be used to steer the properties of individual molecules at surfaces, which I would also like to talk about if time permits. In summary, development of such a strategy opens up new routes to steer on-surface reactions and even single molecule properties in surface chemistry.

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