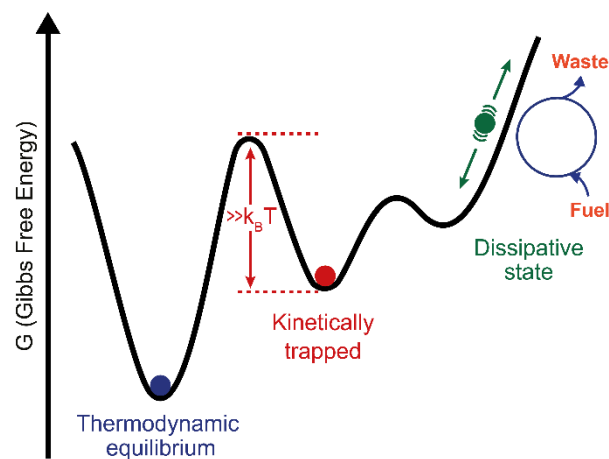


Beyond equilibrium self-assembly: kinetic control and dissipative self-assembly in supramolecular systems

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Self-assembly processes have a key role in the bottom-up fabrication of complex supramolecular structures and advanced functional materials. Traditionally, their control has relied on introducing specific moieties into the building blocks for directing recognition and interaction, while targeting the global minimum of the free energy landscape (*thermodynamic control*).^{1,2} Recently, however, there is a major interest in developing new approaches and methods that can potentially convey an improved spatio-temporal control over molecular self-assembly, with the aim of expanding the toolbox of non-covalent synthesis.³



One approach is to target the kinetically trapped structures that may exist on a complex (multi-well) supramolecular energy landscape, and whose formation strongly depend on the preparation procedure, and assembly pathway(s). That is, by controlling self-assembly kinetics it is possible to steer non-covalent synthesis in the desired direction (*pathway selection*), leading to different supramolecular structures from the same building blocks.² Another more recent strategy is mimicking living self-assembled systems, such as microtubules, which operate in so-called *dissipative non-equilibrium states*, and continuously consume energy to precisely control their supramolecular structure and functions in space and time.^{2,4} Accordingly, new developments in the field of artificial self-assembly involve the use of chemical fuels as energy inputs to drive the assembled systems away from thermodynamic equilibrium.⁵⁻⁸

In this talk, I will discuss and give illustrative examples of non-equilibrium supramolecular systems, both kinetically trapped and dissipative. In the former case, I will show how the precise control of concentration gradients and reaction-diffusion (RD) phenomena achieved within advection-free microfluidic environments facilitates an improved control over self-assembly kinetics and pathway selection.³ In particular, the use of microfluidic conditions has allowed us to: enhance chiral induction in porphyrin aggregates;⁹ control the degree of protonation defects and the magnetic properties of a coordination polymer; mimic two main strategies of morphogenesis in biomineralization,¹⁰ leading to single crystals of a peptide-based metal-organic framework (MOF) with unprecedented non-equilibrium shapes and sizes up to the millimetre range. In the latter case, I will report on a supramolecular polymer, controlled by enzymatic phosphorylation/dephosphorylation, that can be kept in various dissipative non-equilibrium steady states inside a membrane reactor where the chemical fuel ATP is added continuously, while waste is removed.⁸

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