

Photodynamic covalent bonds as a tool to shift reaction networks out-of-equilibrium

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Dynamic Covalent Bonds combine the robustness of regular covalent bonds with the dynamicity of “soft” supramolecular interactions. They serve as a tool to *dynamically* connect different molecular entities, *i.e.* the interconnections easily break and reform resulting in the continuous exchange of the building blocks that form a molecular species and thus in the continuous variation of its properties. Importantly, such a dynamic system minimizes its overall energy and thus approaches an equilibrium state with a constant composition of the individual molecular species. Thereby, under given surrounding conditions (e.g. temperature, pH, or the presence of a binder) the “fittest” species within the evolving library of molecules are preferably expressed. These processes are the basis for self-sorting and self-organization phenomena within complex chemical reaction networks, of which can be found numerous examples in nature.

However, many self-organization processes found in living nature do not approach the overall energetic minimum but evolve within metastable or “out-of-equilibrium” states, which are accessed and held up by consuming energy. Thereby, the out-of-equilibrium state has properties or functions that are inaccessible within the energetic minimum of the system. In contrast, for today’s synthetic chemists it remains a big challenge to construct artificial self-organized dynamic reaction networks that can be driven into out-of-equilibrium states by delivering some kind of energy to the system.

In this context, new “photodynamic” covalent bonds are developed on the basis of photoresponsive alkoxyamines. They dissociate upon activation with light and subsequently reform in a fast thermal back reaction. Thus, while in the dark molecular species containing these bonds are perfectly stable, upon light irradiation dynamic exchange of their building blocks is induced. This allows not only for the precise control over where and when exchange processes take place, but it is shown that photodynamic covalent bonds may serve as an interface to repeatedly drive thermally equilibrated dynamic reaction networks into out-of-equilibrium states using the energy of the applied light (Figure 1).

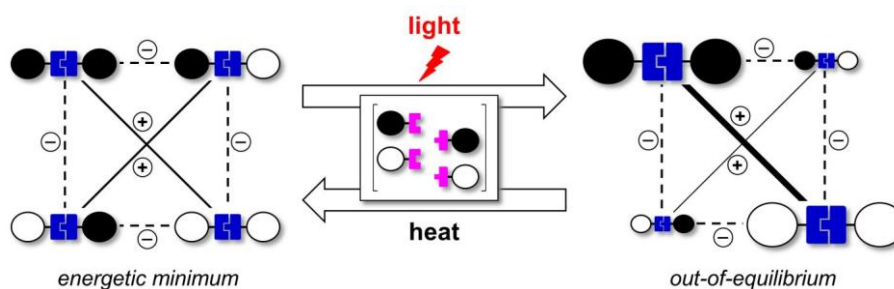


Figure 1: Upon light activated exchange of photodynamic bonds within a dynamic covalent reaction network an out-of-equilibrium state can be reversibly populated, in which specific molecular constituents are amplified.