Building and Overcoming Walls

Stefan Hecht

Department of Chemistry & IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

Email: sh@chemie.hu-berlin.de; URL: www.hechtlab.de

Synthetic chemistry allows for an infinite number of molecules to be created and thereby provides access to new drugs and materials. While the synthetic chemist is not limited in the choice of building blocks but only by imagination, nature has mastered the art of controlling *when* and *where* specific chemical reactions take place as beautifully illustrated by processing and storing information in the brain. Thus chemists should seek to perform chemistry with the highest possible spatial and temporal resolution, which should allow to time reactions, for example in simple cascades or more complex reaction networks, and to localize them, for example in 2D or even 3D patterns. In our research group we are exploiting photoswitchable systems to obtain spatio-temporal control over various processes, materials' properties as well as the function of optoelectronic devices. For this purpose we are exploring light as a highly selective, non-invasive external stimulus in combination with photochromic molecules. Our work is therefore devoted to developing and improving photoswitches and exploring them in various settings to control, i.e. "gate", and power, i.e. "drive", functional molecular systems.

At ArmChemFront 2018 my presentation will focus on the development of photoswitchable systems that engage in dynamic covalent chemistry and allow us to influence and even shift associated thermal equilibria by light. Based on our ability to photocontrol bimolecular reactions we can influence the extent and dynamics of covalent crosslinking in polymeric materials and thereby are able to externally modulate their inherent (thermal) (self)healing properties.[1] More recently, we could realize the first true ON/OFF systems, which allow imine condensation/hydrolysis to be driven by light – even under energetically and chemically disfavored conditions.[2] The latter is possible due to the presence of thermal barriers, i.e. walls, that can only be overcome by electronic excitation as photodynamic equilibria do not obey Boltzmann population.[3] This provides us with a unique tool to force chemical reactions in specific locations and at precise times and therefore should allow us to construct molecular machinery able to act as an assembly line to convert and store light energy as chemical information in specific products.

[1] M. Kathan, P. Kovaříček, C. Jurissek, A. Senf, A. Dallmann, A. F. Thünemann, S. Hecht, *Angew. Chem. Int. Ed.* **2016**, *55*, 13882.

[2] M. Kathan, F. Eisenreich, C. Jurissek, A. Dallmann, J. Gurke, S. Hecht, *Nat. Chem.* DOI: 10.1038/s41557-018-0106-8.

[3] M. Kathan, S. Hecht, Chem. Soc. Rev. 2017, 46, 5536.