Anion-π catalysis induced epoxide-opening ether cyclizations on different surfaces

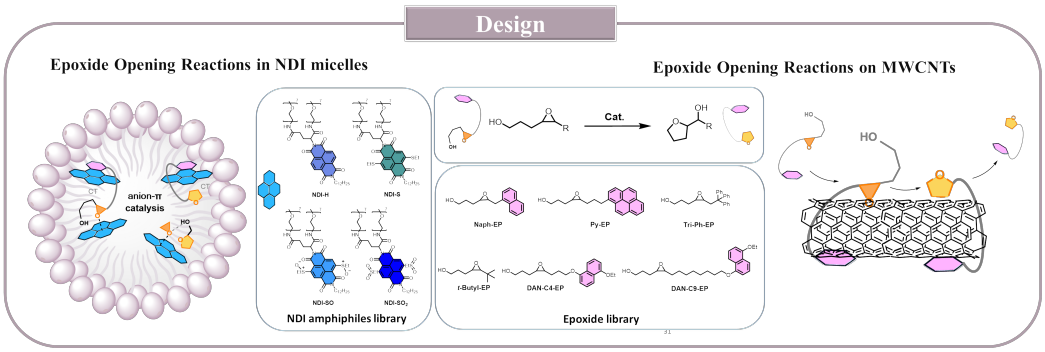
M. Tan[1], M. Gutiérrez López[1], N. Sakai[1], S. Matile[1]*

[1]Department of Organic Chemistry, and University of Geneva, 1211 Geneva, Switzerland

Anion-π catalysis, that is the stabilization of anionic transition states and reactive intermediates on π acidic aromatic surfaces, is rare in nature and has been ignored for a long-time in chemistry.[1] Since anion-π catalysis was reported in 2013 firstly, with the enolate addition chemistry in place, anion-π catalysts up to π-stacked foldamers, fullerenes and carbon nanotubes could be developed, which then were used to realize different reactions like asymmetric enamine, iminium, Diels-Alder, transamination or epoxide-opening chemistry [1,2].

Naphthalenediimides (NDIs) are well known by its π-acidity when different electron withdraw substituents were installed on its core structures, and the anion-π interaction promoted autocatalysis of epoxide-opening ether cyclizations was first observed on sulfone-NDI derivatives[2]. Herein reported anion-π catalysis in various NDI micelles (e.g., sulfoxide, sulfone) which could provide a space-confined and solvent-free environment in where epoxides could become more concentrated and pre-organized, so that significant rate enhancement and autocatalytic behavior were realized when compared with reactions either in organic solvents or other surfactants.

Meanwhile, carbon nanotubes were known for its induced π acidity in response to the binding of anions or anionic transition states due to the repulsion of the nearby π electrons toward the other end of the π system, thus enabling and strengthening anion binding on the π surface[3]. Therefore, MWCNTs have been applied in our work to serve as a powerful anion- π catalysts due to their high polarizability. And further electronic field assisted anion-π catalysis on MWCNTs surfaces was also proved promising and practical.



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