

Developing Non-Native Cascade Reactions by Means of Catalytic Nanocompartments

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Compartmentalization is fundamental in nature, where the spatial segregation of biochemical reactions within and between cells ensures optimal conditions for the regulation of cascade reactions. Reproducing, but also manipulating hierarchically organized compartments with regard to their responsiveness and communication provide crucial information towards understanding biological systems. One of the most promising strategies to mimic nature compartmentalization is to combine synthetic nano-compartments with biomolecules in order to develop artificial organelles and to organize them into more complex architectures with cell mimetic functionality.

We present an exquisite spatiotemporal control of catalysis in polymeric nanosized compartments by means of a periodate sensitive linker that controls the opening of outer membrane protein OmpF (OmpF) channels inserted in the compartment membrane.[1] Being able to precisely time confined reactions pave the way to controlling multifunctional cluster activity when specific substrates or products need to be made available at a specific site and with precise timing.[2] In addition, the combinatorial and functional diversity of catalytic nanocompartments (CNCs) assembled into various supramolecular architectures can be exploited either in bulk or on a surface, whereby surface immobilization offers the advantage of highly controlled spatial organization. As an example, we developed CNC-functionalized DNA microarrays where individual reaction compartments are kept in close proximity by a distinct geometrical arrangement to promote effective communication.[3] Our work represents a significant advance in the field of communicative networks by combining compartmentalization with controlled inter-compartment distance to promote efficient cascade reactions.

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[2] V. Maffeis, A. Belluati, I. Craciun, D. Wu, S. Novak, C.-A. Schoenenberger, C. G. Palivan, *Chem. Sci.* **2021**, 12, 12274.

[3] V. Maffeis, D. Hürlimann, A. Krywko-Cendrowska, C.-A. Schoenenberger, C. E. Housecroft, C. G. Palivan, *Small* **2022**, 2202818.