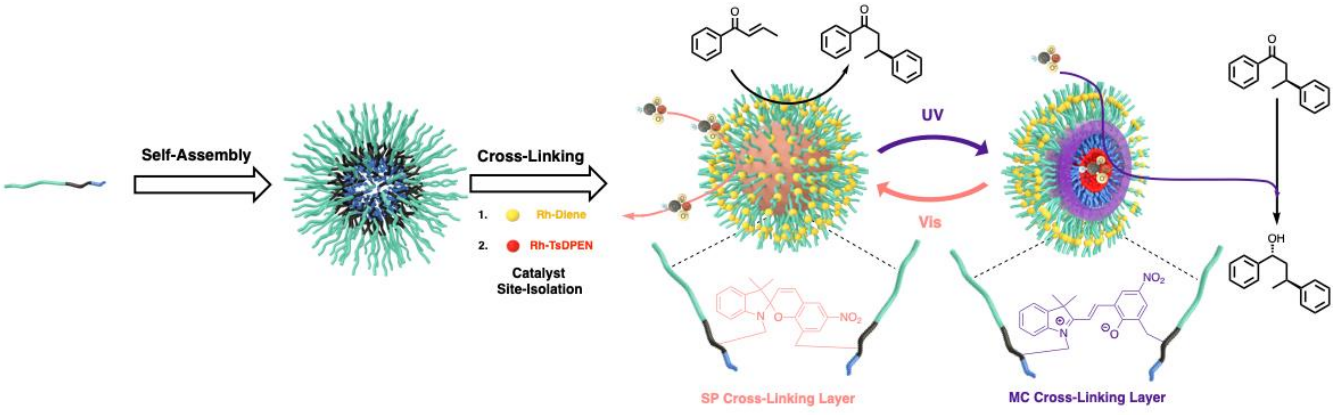
Photo-responsive polymeric nanoreactors for compartmentalization and photo-regulation of incompatible tandem catalysis

Peiyuan Qu[1] and Marcus Weck[1]

1. New York University, New York, New York, United States

One of the paramount goals in modern science is to design and realize artificial nanostructures that rival biological systems in terms of complexity, functionality, and efficiency. The cell perfects the regulation of thousands of incompatible chemical transformations simultaneously using key concepts such as compartmentalization of active sites and communication between compartments.
Inspired by nature, this presentation will introduce an advanced compartmentalized polymeric nanoreactor that possesses a reversible photo-responsive feature and can photo-regulate reaction pathways for incompatible tandem catalysis. The smart nanoreactor is based on multi-functional amphiphilic poly(2-oxazoline)s-based micelles, covalently cross-linked with a bifunctional spiropyran. The smart nanostructure responds to light irradiation in a wavelength-selective manner and switches its physicochemical properties i.e. color, hydrophobicity, and size as confirmed by dynamic light scattering and cryo-transition electron microscopy. The tailor-made microcompartments within the nanoreactor render distinct yet suitable environments for two incompatible enantioselective transformations: a rhodium-diene complex-catalyzed asymmetric 1,4-addition occurs in the hydrophilic corona and a Rh-TsDPEN-catalyzed asymmetric transfer hydrogenation reaction in the hydrophobic core. A series of control experiments and kinetic studies shows that the gated behavior induced by the photo-triggered reversible spiropyran to merocyanine transition in the cross-linking layer is key to discriminate among substrates/reagents during the catalysis. The smart nanoreactor has realized photo-regulation to direct the reaction pathway to give a multi-chiral product with great conversions and perfect enantioselectivities. Our smart polymeric catalytic system, on a basic level, mimics the concepts of compartmentalization and responsiveness Nature uses to coordinate thousands of incompatible chemical transformations into a streamlined metabolic process.



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