

University of Louisville  
Department of Chemistry

## Uyen Duong Research Seminar

When: November 5, 2020

Time: 2:30 PM

Location: Microsoft TEAMS

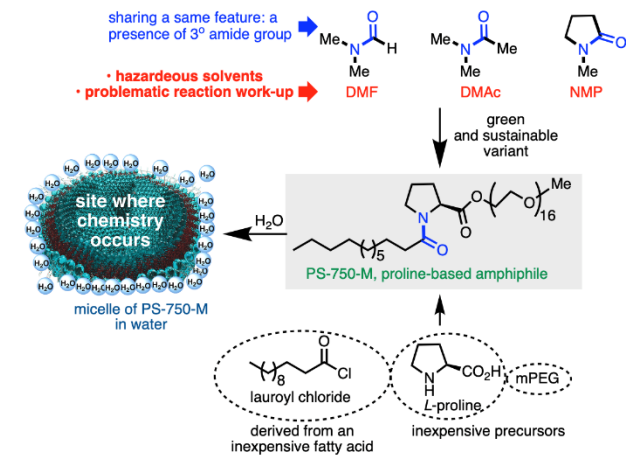
# Reactive Intermediates in Aqueous Micelles for Better Chemistry

## Abstract

Water is considered as green, sustainable, and inexpensive solvent for organic synthesis.<sup>1,2</sup> However, performing organic reactions in water is especially challenging due to the inherent insolubility of substrates and catalysts. Inspiring from Nature where chemistry happens in water, micellar catalysis has recently gained much attention, especially for the pharmaceutical industry's applications. Aqueous micelles are generally formed by amphiphiles' self-aggregation, a particular class of organic molecules possessing both hydrophobic and hydrophilic components. The aqueous micelle contains a hydrophobic cavity, which allows the lipophilic substrates and catalyst to go inside micelles, allowing their much higher localized concentration that enhance the reaction rates and improves purity profile.<sup>3,4</sup> Following Nature's lead, our group has developed a proline-based amphiphile PS-750-M that mimics dipolar-aprotic solvents, such as 1,4-dioxane, DMF, DMAc, and NMP.<sup>5,6</sup> Although we have reported better reactivity of many-valued transformations in PS-750-M, the fundamental understanding of reaction intermediates' reactivity, such as carbenes, carbanions, and radicals are yet untouched topics. The knowledge on the reactivity of such intermediates under the shielding effect of micelles could open new research avenues, in particular, for the design of more unique and challenging reaction pathways.

In this seminar, the reactivity of carbenes and radicals in aqueous PS-750-M will be discussed. In particular, palladium nanoparticles ligated with inexpensive triphenylphosphine and amphiphile PS-750-M are suitable for exploring the reactivity of carbenes in aqueous nanomicelles. Our ligated-nanoparticles found to be highly selective for metal-carbene migratory insertion while micelles PS-750-M shields the in-situ generated carbene to prevent the dimerization. In addition to broad substrate scope, the nanocatalyst is thoroughly characterized by NMR, SEM, HRTEM, XPS, and TGA. The sustainability of the reaction system is demonstrated by the recyclability of both the nanoparticle catalyst and the micellar reaction medium at variable reaction scales. NMR and kinetics studies with the recycled catalyst revealed the retention of catalyst integrity. Control experiments including DLS study demonstrate the importance of PS-750-M.<sup>7</sup>

Likewise, to explore the reactivity of persistent radicals, we have developed a catalyst that by design, forms nanochannels through which substrate containing micelles could travel to enable the desired chemistry. For example, upon visible-light irradiation, our in-house designed heterogeneous polymer of PDI-Cu(I)-PDI generates charge transfer states that are subsequently quenched by molecular oxygen for their participation in redox activity. This insoluble polymeric Cu(I) is catalytically active for the oxidation of alcohols to aldehyde when suspended in dynamic micelles of PS-750-M. A broad substrate scope, excellent selectivity, and no over-oxidation reveal the catalyst robustness. The catalytic activity, control experiments, and time-dependent DFT calculations show the charge transfer states. The polymeric catalyst is entirely recyclable, as evidenced by the recycle studies using recyclability test. The morphology, structure, copper's oxidations state, and the catalyst's thermal stability are determined by SEM, XPS, and TGA analysis.<sup>8</sup>



## References

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