

University of Louisville
Department of Chemistry

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Research Seminar

When: April 21, 2022

Time: 12:00 p.m.

Location: CBLL-16

New Methodologies for Sustainable Organic Synthesis in Water

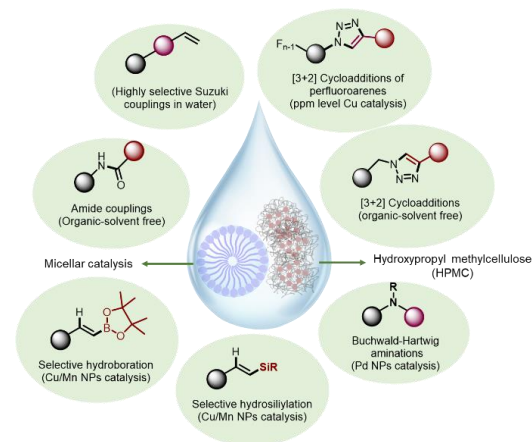
Abstract

Water is stable, benign, and green solvent. The use of water as a solvent in organic synthesis is significantly enabled by micellar catalysis.¹ However, replacing water as a reaction medium in organic synthesis is insufficient to meet the sustainability challenges—excessive organic solvents are still required for product isolation and purification. Solvents used in syntheses contribute to more than 80% of waste generation.² In addition to solvents, the use of palladium (Pd) and copper (Cu) in large amounts is also a problem for the future as it is an endangered metal, and its economically accessible supply is dwindling. Therefore, the research talk will focus on the minimization of usage of solvents, Cu, and Pd for amide couplings, cycloaddition reactions, and cross-couplings, respectively.

The first part of the talk will highlight the use of our designer surfactant PS-750-M, which structurally mimics toxic dipolar-aprotic organic solvents, such as DMF, DMAc, and NMP. PS-750-M, along with the coupling agent, forms mixed micelles, which enable ultrafast amide couplings in water.^{3,4} The most common coupling agent used in amide couplings is 1-Ethyl-3-(3-(dimethylamino)propyl)-carbodiimide (EDC•HCl). It has lipophilic and hydrophilic regions, allowing its self-aggregation in an aqueous medium containing PS-750-M to form mixed micelles. These mixed micelles provide a high local concentration of reactants, resulting in ultrafast reaction rates without product epimerization. The methodology completely avoids any organic solvents as the product spontaneously extrudes from micelle, allowing its isolation by simple filtration.

Next, sustainable and inexpensive Cu(I) catalysis will be discussed. Notably, spontaneous oxidation of Cu(I) to Cu(II) adversely affects the reaction efficiency.⁵ We developed a catalytic methodology that uses Cu(II) nanomaterial, light, and azide. The irradiation triggers the single electron transfers from azide to Cu, generating Cu(I) species within the micelles to enable powerful cycloaddition chemistry via Cu(I) catalysis. Nanomaterial was characterized using XAS, HRTEM, NMR, UV-Vis, and IR spectroscopy. In addition, a completely organic solvent-free technology using hydroxypropyl methylcellulose (HPMC)⁶ will be elaborated for Cu(I) catalysis.

The last part of this talk will describe the development of new (bi)trimetallic nanoparticles (NPs). These NPs exhibit the synergy between two or more metals that enable robust, sustainable, and selective catalysis. The bimetallic NPs of Cu and Mn, as well as trimetallic NPs of Cu, Mn, and Pd, enabled selective Suzuki-Miyaura cross-coupling, hydroboration, and hydrosilylation of alkenes, alkyne, and chalcones.



References

- 1) T. N. Ansari, S. Handa, F. Gallou, in *Organometallic Chemistry in Industry, A Practical Approach*, Wiley, 2020, pp. 203.
- 2) D. J. C. Constable, C. Jimenez-Gonzalez, R. K. Henderson, *Org. Process Res. Dev.* **2007**, *11*, 133.
- 3) S. Sharma, G. Kaur, S. Handa, *Org. Process Res. Dev.* **2021**, *25*, 1960.
- 4) S. Sharma, N. W. Buchbinder, W. M. Braje, S. Handa, *Org. Lett.* **2020**, *22*, 5737.
- 5) G. Anilkumar, S. Saranya, in *Copper Catalysis in Organic Synthesis*, Wiley, **2020**, pp 1.
- 6) S. Sharma, T. N. Ansari, S. Handa, *ACS Sustain. Chem. Eng.* **2021**, *9*, 12719.