

Addressing diffusion in the solid photo- and photoelectrocatalysts

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**Chemistry
Seminar on
Photo- and
Photo-
electrocatalysis
using MOFs**

**Monday
Feb. 20 at 4
pm in 303
Schrenk**

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Abstract: Light-driven reactions hold promise to develop processes that can encompass solar energy conversion, organic transformation, to contamination management. To ease the transformations that are energetically challenged or otherwise not thermally allowed—like, kinetically challenged CO₂ reduction, organic transformations involving C-H activation, or thermally inaccessible cycloaddition reactions—one needs to build an efficient deployable photocatalysts platform. Traditional solution-dissolved photosensitizers, exploiting their long-lived triplet state, function by providing a time window for slower diffusion and chemical time scale. However, special care must be taken even for those reactions that do not require a triplet excited state (like cycloaddition) to avoid singlet oxygen-derived side products.

The primary criteria for scalable solid photocatalysts are challenging: it requires efficient exciton/energy transport to the reaction sites and the ability to split the delivered exciton without the involvement of molecular (i.e. photosensitizer) diffusion. This is simply because of fixed photosensitizers where only a small portion, at the outer surface, is exposed to the light. A porous solid, such as a MOF system that allows substrates to diffuse, can only work if the molecular excitons are spatially dispersed and/or easy to displace -possibly along the direction of the major substrate diffusion channel (i.e. anisotropic exciton transfer). System design with the appropriate ground and excited-state potential will, therefore, be the next step to driving a redox reaction. A picosecond timescale exciton transport and subnanosecond timescale exciton splitting should be the primary target to develop such a platform. With such a design in hand, we will show how MOF-based photoredox chemistry works and what are other benefits of this development.

About the speaker: Deria carried out his first experiment in 2020 summer at JNCASR and IISc Bangalore India trying to make enantioselective epoxidation and MOLY-base sugar functionalization. He then worked on developing heterogeneous catalysts for phosphate ester toxin decompositions at IIT Kanpur. Fascinated by the photoinduced processes and catalysis, he went on to study molecular and nanoscale assemblies. Initially, this involved developing covalent, coordination-chemistry-derived, and noncovalent (functionalization) strategies to prepare tailor-made molecular and macromolecular assemblies. His doctorate studies at Penn involved ionic conjugated polymer-wrapped SWNT assemblies and their optoelectronic properties. His postdoctoral tenure at Northwestern involved developing a widely used MOF-functionalization method called Solvent-Assisted Ligand Incorporation (SALI). His current research includes developing porous solids for photo-, electro-, and photoelectrocatalytic transformations and energy conversion. Research on developing efficient artificial light-harvesting antenna systems received *NSF CAREER*, whereas heterogeneous selective photoredox chemistry is supported by NIH. These researches fundamentally address how to manipulate molecular excitons in the solid assembly. He was tenured in 2021 July at SIU.