



Exciton Dynamics of Zr-Based MOFs Toward Photoredox Catalytic Organic Transformations

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Abstract:

Natural light-harvesting systems in plants rely on precise chromophore positioning and inter-chromophore interactions that direct excitation energy to the reaction center. Inspired by this, we designed zirconium- based metal–organic frameworks (MOFs) incorporating Zr_6 nodes and strongly absorbing chromophores such as pyrene, porphyrin, and anthracene. The Zr nodes are optoelectronically inert, enabling the intrinsic photophysics of the linkers to dominate.

Within these MOFs, linker assemblies exhibited coherent singlet excited states, wherein trimeric units shared exciton energy^[1]. This coherence suppressed intersystem crossing despite the triplet-active nature of the free linkers and generated polar states through symmetry-breaking charge transfer (SBCT), probed via solvent-dependent pump–probe spectroscopy^[2]. To reintroduce triplet formation, we employed palladium–porphyrin linkers that provided inner-sphere heavy atom effects. Depending on topology, compact microporous frameworks displayed short-lived triplets limited by strong triplet–triplet annihilation, while mesoporous analogues generated long-lived triplets persisting over microseconds^[3]. In parallel, anthracene-based linkers were used to study topology-dependent singlet fission in MOFs achieving triplet yield over 100 percentage^[4,5].

These fundamental insights were applied to photocatalysis, using the MOFs as photosensitizers in aerobic aza-Henry reactions of N-aryl-tetrahydroquinoline derivatives. The frameworks achieved half-conversion within ~ 3 h and turnover frequencies $> 100 \text{ h}^{-1}$, outperforming conventional triplet excited state-based

benchmarks and highlighting the catalytic potential of singlet-excited states^[1]. Systematic studies across fourteen amine substrates revealed the influence of solvent dielectric constant, light fluence, and substrate oxidation potential. Mechanistic analysis indicated a cascade initiated by photoinduced electron transfer to form amine radical cations and superoxide, followed by hydrogen atom transfer or proton abstraction pathways.

References;

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Biography: Sreehari was born and raised in Kerala, India, where he developed an early fascination with chemistry and science. He went on to pursue a BS-MS dual degree at the Indian Institute of Science Education and Research (IISER) Trivandrum, majoring in Chemistry with a minor in Physics. During his time at IISER, he gained research experience in both materials chemistry and experimental physics, working on metal-organic frameworks (MOFs) and gold nanoclusters.

In Fall 2019, he joined the Chemistry PhD program at Southern Illinois University Carbondale (SIUC). He has been working under the guidance of Prof. Pravas Deria to investigate exciton dynamics and photoredox reactivity in MOF-based systems using advanced spectroscopic techniques. At SIU, Sreehari has contributed to multiple research projects, contributed to 15 peer-reviewed publications, mentored high-school and undergraduate students, and taught several chemistry laboratory courses. His work focuses on understanding excited-state processes in supramolecular assemblies and developing light-driven catalytic platforms.

Outside the lab, Sreehari enjoys cooking, working out and watching anime.