Abstract: Photochemical reactions are increasingly important for the construction of value-added, strained organic architectures. Direct excitation and photoredox reactions typically require mild conditions and permit access to highly strained molecules and new synthetic methodologies. The a priori design of photochemical reactions is challenging because degenerate excited states often result in competing reaction mechanisms to undesired products. Further, a lack of experimental techniques that provide atomistic structural information on ultrafast timescales ($10^{-13} - 10^{-12}$ s) limits general 'chemical intuition' about these processes. Computations, however, provide a path forward. I will discuss how my group has leveraged state-of-the-art quantum mechanical calculations, non-adiabatic molecular dynamics, and machine learning (ML) techniques to understand the reactivities and selectivities of a photochemical cascade reaction towards the first stable polyacetylene, fluoropolyacetylene. I will introduce our new open-access machine learning tool, Python Rapid Artificial Intelligence Ab Initio Molecular Dynamics (PyRAI²MD), which enables 1,000-fold longer simulations than are currently possible with multiconfigurational NAMD simulations. PyRAI²MD has enabled nanosecond ML-NAMD simulations on stereoselective electrocyclic reactions with record degrees of freedom and molecular complexities.