“A Synthesis-Driven Approach to Opto-Electronic and Chiroptical Molecular and Supramolecular Materials”

Abstract. The versatile, click-chemistry-type [2+2] cycloaddition-retro-electrocyclization (CA-RE) cascade between donor-activated alkynes and electron-accepting olefins has enormously widened the chemical structure space for push-pull chromophores. This high-yielding, atom-economic, thermodynamically driven transformation affords highly soluble, stable non-planar donor-acceptor chromophores with efficient third-order optical nonlinearities, which have successfully been tested in silicon-organic-hybrid devices for all-optical processing, enabling THz optical switching. Some of the new chromophores, which also include a diversity of 6,6-dicyanopentafulvene derivatives, are “super acceptors”, with the first reduction occurring at positive potentials (against ferrocene, in CH$_2$Cl$_2$), and form intermolecular charge-transfer complexes with metallocene donors. The CA-RE reaction also works on the central “proacetylenic” C=C bond of [3]cumulenes which provides access to novel dicyano-diaryl-substituted tetracenes with a rubrene-like substitution pattern by a 2-step protocol. They can be used as fluorescent chemosensors for soft metal ions. Most recently, Wasielewski and co-workers measured efficient, sub-picosecond singlet exciton fission in thin-films of these systems.

Optically active, acyclic and macrocyclic allenoylacetylenes feature exceptionally intense Cotton effects in their electronic circular dichroism (ECD) spectra. We further derivatized these unique building blocks for use as supramolecular materials. An enantiopure, shape-persistent allenoylacetylenic macrocycle, peripherally decorated with eight phenolic rings, stacks in the solid state to form chiral channels capable of guest inclusion. The phenolic side groups have been decorated with additional mesogenic side chains and stable, tubular self-assembly was evidenced by Cryo-TEM in aqueous solution. Triple helicates of enantiopure phenanthroline-terminated allenoylacetylenes form in the presence of Zn(II) ions, which are efficient chiroptical sensors (induced circular dichroism, ICD) for encapsulated non-chromophoric achiral guests, such as cycloalkanes and heteroalicycles.