

# **Organic Semiconductor Heterojunctions for Solar Energy Conversion**

**Frédéric Laquai**

**King Abdullah University of Science & Technology (KAUST), KAUST Solar Center (KSC)**

Organic semiconductor heterojunctions, consisting of polymeric and small molecule donor and acceptor materials with offset energy levels, have garnered significant attention as photoactive systems for photovoltaic (PV) and photocatalytic (PC) energy conversion processes. However, as molecular low dielectric constant semiconductors, their primary photoexcitations are strongly-bound electron-hole pairs (Frenkel-type excitons), which can only be separated into free charges at the cost of an 'energy penalty.' Moreover, carrier recombination processes and inherent energy losses in disordered materials remain bottlenecks for further efficiency improvements.

In the first part of the talk, I will discuss recent results on efficiency-limiting processes in state-of-the-art non-fullerene acceptor (NFA) photovoltaic devices obtained by using steady-state and advanced transient optical and electro-optical spectroscopies. While the mechanism leading to efficient charge photogeneration in fullerene-based blends has been extensively studied, processes occurring in NFA-based solar cells are still less clear. In many NFA-based systems, efficient energy transfer from the donor to the acceptor precedes charge transfer, causing a dependence of the devices' internal quantum efficiency primarily on the heterojunction's ionization energy (IE) offset. The required IE offset has been debated extensively, with values ranging from zero or even negative offsets to hundreds of meVs, depending on the experimental techniques used to determine the energetic landscape of organic semiconductors. A better understanding of such intrinsic limitations is a prerequisite for computational (in-silico) approaches to material design. Furthermore, I will demonstrate that spectroscopically determined parameters, including rate constants and process yields of fundamental photophysical processes, can accurately reproduce experimentally measured device characteristics.

In the second part of the talk, I will present recent results on using organic semiconductors in bulk heterojunction nanoparticles decorated with noble metals as a cocatalyst for photocatalytic processes such as water splitting and carbon dioxide reduction in nanoparticle suspensions under visible light excitation. Recent work has shown that photocatalytic conversion efficiencies can exceed those obtained with inorganic photocatalysts in both hydrogen generation and carbon dioxide reduction. However, similar to photovoltaic devices, photocatalytic conversion efficiencies are limited by incomplete exciton quenching and limited carrier funneling to the catalytically-active sites, as well as nanosecond to microsecond charge carrier recombination. In addition, nanoparticle preparation and cocatalyst deposition conditions tremendously affect photocatalytic efficiencies and limit the yield of photocatalytically active nanoparticle batches. Despite these constraints, the study successfully demonstrates selective carbon dioxide to methane or carbon monoxide conversion, depending on the specific nanoparticle composition and cocatalyst used, while largely suppressing proton reduction, often occurring as an unwanted side reaction.