Electronic Interactions in Hybrid Organic-Nanoparticle Materials

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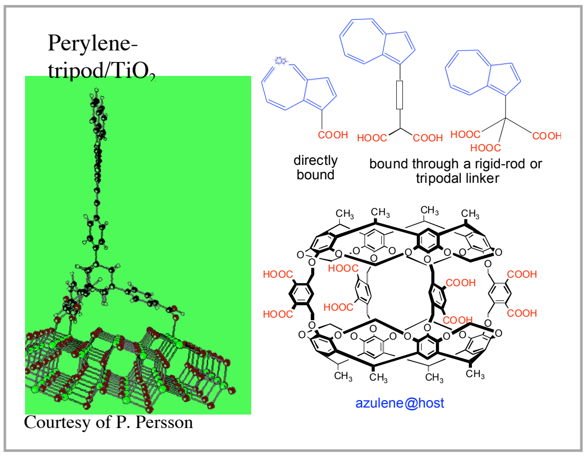
The goal of this research program is to control and understand electronic interactions at the interfaces between molecules and semiconductor nanoparticles through photophysical studies of hybrid organic-nanoparticle materials. These are organic dyes covalently attached to the surface of the semiconductor though rigid linkers with the shape of tripods or rods (tripod/TiO_2 or rod/TiO_2), as well as dyes incapsulated in molecular containers that bind to the semiconductor through multiple points of attachment (dye@host/TiO_2). In particular, the NIRT team's current studies involve a variety of tripodal and rigid-rod linkers capped with pyrene, azulene, and other organic chromophores as well as azulene@host bound to films or colloidal solutions of semiconductors nanoparticles (TiO_2, ZrO_2, ZnO) though anchoring groups (carboxylate, phosphonate): ***(1)*** The study of ultrafast long-range electron injection from the dye into the semiconductor through conjugated bridges ('molecular wires') utilizing the new sub-30 fs laser system consisting of two noncollinear optical parametric amplifiers. ***(2)*** The study of the formation of excimers and the effect on injection processes and on solar cells efficiencies. The NIRT team is developing methods to prevent and control aggregation of organic dyes, including the use of tripodal linkers with a large footprint. ***(3)*** The formation of azulene@host/TiO_2 was probed by fluorescence quenching and the formation of azulene$^{\cdot+}$@host/TiO_2 resulting from the electron injection TiO_2 was confirmed by transient absorption measurements. Single exponential recombination kinetics was observed, in contrast with any known recombination processes on TiO_2 which exhibit complex nonexponential behavior, possibly an effect of the "molecular insulation" of each dye molecule by encapsulation in the molecular container. Comparison is now being made with azulenes bound through linkers. ***(4)*** The NIRT team is working to identify and characterize favorable binding configurations of different linkers to the semiconductor nanoparticles and is studying with Prof. P. Persson at Uppsala University in Sweden the roles of the anchor and linker groups as mediators (or barriers) for interfacial heterogeneous electron transfer.



Other aspects of the project are studied through international collaborations that are possible thanks to the foreign travel supplement to the NIRT grant: ***(5)*** The inhomogeneity of a sensitizer binding to TiO_2 surfaces was investigated in time-resolved confocal fluorescence microscopy experiments performed in collaboration with the group of Prof. Johan Hofkens at the University of Leuven. ***(6)*** Prof. Frank Willig at the Hahn-Meitner-Institut in Berlin is studying a perylene tripod/TiO_2 to probe the distance dependence of electron injection in perylene dyes by ultrahigh-vacuum-ultrafast laser spectroscopy, and has demonstrated through polarized fluorescence studies on flat rutile that the tripod binds perpendicularly.

References: For further information about this project contact galoppin@andromeda.rutgers.edu (http://www.andromeda.rutgers.edu/~galoppin/) meyer@jhu.edu (http://www.jhu.edu/~chem/meyer/meyer.html) or piotr@andromeda.rutgers.edu (http://andromeda.rutgers.edu/~piotr/piotr.html).