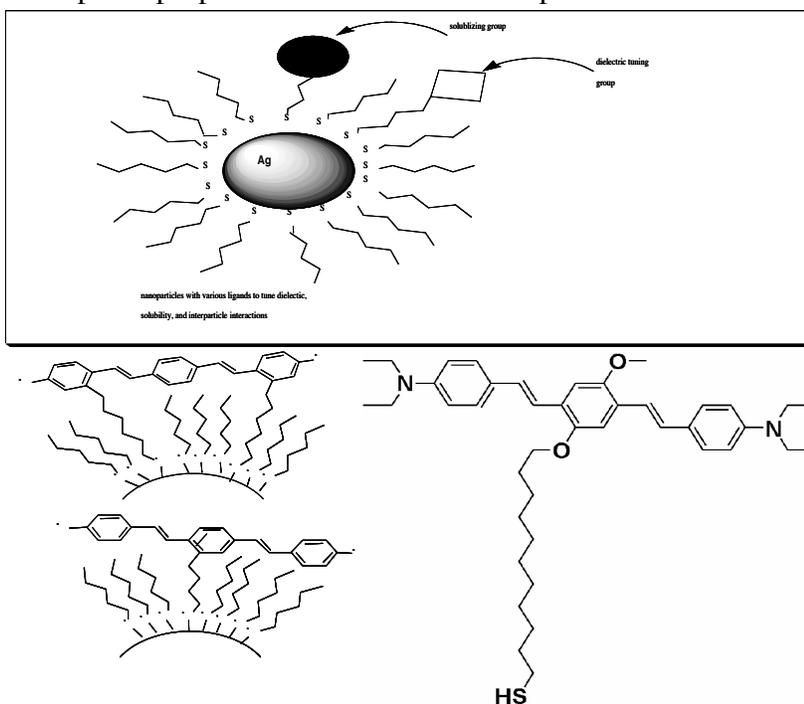


Optical and Electronic Processes in Metal Nanoparticle-Conjugated Organic Materials
T. Goodson III, J. Perry, S. Marder, B. Kippelen, F. Stellacci
University of Michigan, Georgia Inst. of Technology, Massachusetts Inst. of Technology

The research in this NIRT program consists of synthesis, microscopic characterization, nonlinear and time-resolved optical spectroscopy, and device fabrication of novel metal particles coated with organic chromophores. A fundamental objective of the research is to analyze the metal (plasmon) and chromophore (orbital) interactions which may facilitate enhanced linear and nonlinear optical properties and to utilize these processes in devices.

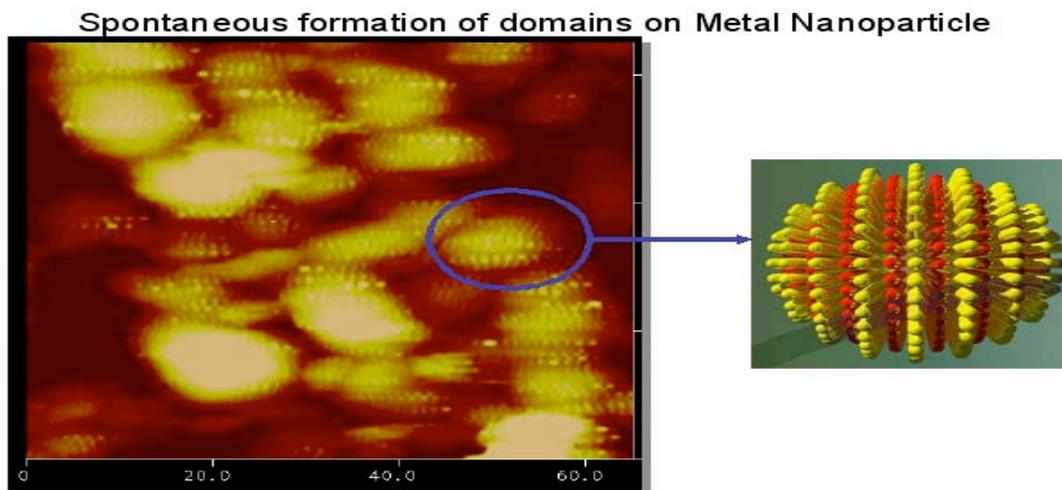
One of the applications we are interested in addressing in this NIRT program is the enhanced two-photon absorption (TPA) properties in organic chromophores attached by various ligands to metal nanoparticles. TPA materials have been used in applications such as imaging and sensor and eye protection devices. A particular class of organic chromophores based on substituted distyrylbenzene units



was investigated initially. The synthesis and characterization of the systems was carried out by Marder et. al. These chromophores have shown impressive TPA cross-sections and interesting emission properties in solution and in the solid state. By use of alkane-thiol ligands these chromophores were assembled on to silver metal nanoparticles with relatively narrow particle diameter distributions. The number bis(diethylamino)-bis(styrylbenzene) thiolated dyes per particle determined using elemental analysis and TEM particle size measurements is 2200 +/- 480. With direct feedback from optical and device investigations of these metal particle-organic chromophore systems future systems will be prepared to probe the important structure-function relationships.

With samples similar to the prepared metal particle-organic chromophore materials scanning probe microscopy has been carried out by Stellacci et. al. In these and related experiments it was found that the morphology of the attached ligand-chromophore system is controlled by the particle's radius of curvature and is different from the morphology for which the same ligand assumes on flat surfaces. In particular, it was found that metal nanoparticles coated with mixture of different types of ligands show ordered, phase-separated domains at an unprecedented molecular length scale. Scanning tunneling and transmission electron microscopy images of monolayer protected metal

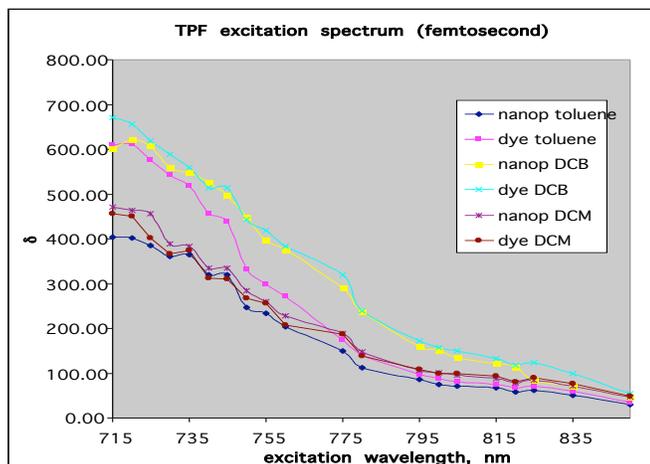
nanoparticles (MPMNs) with ligand shells composed of a binary mixture of molecules show that the ligands phase-separate into ordered domains spaced < 1 nm. Importantly, the domain shape and dimensions can be controlled by varying the ligand composition or the metallic core size. It was also found that the formation of ordered domains depends



on the curvature of the underlying substrate. The information from the microscopy results helps strengthen our hypothesis that the novel properties observed from optical spectroscopy (and later device properties) may result from this nanostructuring of the organic chromophores on the metal particle.

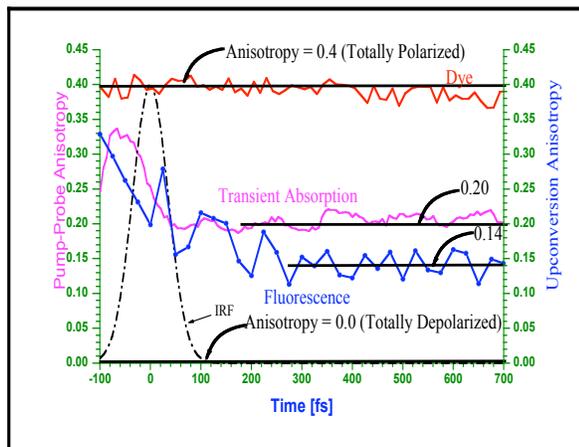
Investigations of the distyrylbenzene chromophore metal particle system's linear and TPA optical properties were carried out by Perry et. al. The fluorescence of the chromophore in the presence of the metal particle attachment is quenched by factors of 1.6 to 2.4 depending on solvent. Calculations based on experimental yields and lifetimes indicate that in toluene the nonradiative rate increases by a factor of 5 but the radiative rate decreases by a factor of 2 and this combination gives an overall reduction of yield by 2.4, with the lifetime almost constant. The increase in nonradiative rate is most likely due to energy transfer to the nanoparticle. The decrease in radiative rate could be due to a plasmon reduction of the local field effect.

Investigations of the TPA properties were carried out over the two-photon excitation spectrum. Measurements of both the dye and metal particle-dye solutions were investigated and the cross-sections were calculated. It was found that when comparable number densities of chromophores were used the cross-sections were very similar for the dye solutions and the metal particle-dye solutions. Again, this was surprising as the high density



of chromophores as well as the close interaction length of the dipolar chromophore to the metal particle appeared to have a small effect on the magnitude of the nonlinear cross-section. While the interaction was not observed, for the case of dye-metal particle solutions, it was found that the absolute value of the TPA cross-sections was very large ($\sim 10^6$ GM), suggesting that a very large number of chromophores could be assembled in this manner and the additive nature of the increase in cross-section as a function of chromophore density may be extended.

In order to probe the interaction of the chromophores with themselves and with the silver metal nanoparticles, time-resolved measurements were carried by Goodson et. al. Ultra-fast fluorescence and transient absorption anisotropy decay measurements were used to probe fast energy migration processes as well as orientational effects of the chromophores assembled on the metal particles. A fast anisotropy decay result for both the fluorescence and absorption anisotropy decay suggested that there may be an orientational or energy migration process involved in the excitation of the chromophores on the surface of the particle. A relatively high residual anisotropy value was obtained indicating that polarization is retained at longer times and that there is still a degree of local order of the chromophores on the metal nano-particle.



The educational and outreach activities of this NIRT program have been active at all of the locations of the program. In a collaborative manner projects at both Georgia Institute of Technology in Atlanta and at Wayne State University in Detroit have been carried out with summer students from near by high schools. The program at Georgia Tech has also included the use of a state-of-the-art device fabrication facility (Kippelen). The program at

Wayne State University allowed several summer high school students to do research in conjunction with a summer training program to prepare students for college entrance exams and for some of the general (freshman) courses taken in college. These opportunities will continue with Goodson at his new institution. The NIRT group has also focused on educating new scientist in the area of nanotechnology. Stellacci has developed a course entitled "Nanoscale Materials" in which he teaches about nanoparticles, nanowires and nanotubes in this regard.

References

- a) For information about this NIRT project contact Theodore Goodson (tgoodson@umich.edu), Joe Perry (joe.perry@chemistry.gatech.edu), Seth Marder (seth.marder@chemistry.gatech.edu), Bernard Kippelen (bernard.kippelen@ece.gatech.edu), Francesco Stellacci (frstella@mit.edu).
- b) A. Jackson, J. Myerson, F. Stellacci, "Spontaneous assembly of sub-nanometer-ordered domains in the ligand shell of monolayer-protected nanoparticles", *Nature Materials*, 3, 330-336, **2004**.
- c) T. Goodson, O. Varnavski, Y.Wang, "Optical properties and applications of dendrimer-metal nanocomposites" *Inter. Rev. of Phys. Chem.* 23, 109-150, **2004**.