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<th>Nonlinear Optical Properties of Novel Organic Dendrimers and Dendrimer Metal</th>
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Summary of Important Findings During the Period of Support from the Army Research Office

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Progress Summary

During the course of a Young Investigator Award from the Army Research Office (Materials Program) the research in the PI's group has developed into three different but related areas of scientific discovery. The first of these areas concerns the optical properties of novel transition metal nanoparticle topology which we call "Dendrimer Metal Nanocomposites". This novel metal nanoparticle system was investigated under support by the ARO for novel optical limiting and enhanced metal emission properties. We found in particular that gold-metal dendrimer nanocomposites have very strong optical limiting properties that may be useful for eye and sensor protection devices in the visible and near Infrared spectral regions. The emission properties of both and silver dendrimer metal nanocomposites were also investigated by time-resolved upconversion spectroscopy. From these measurements the PI's group found that the efficiency at emission was enhanced in comparison to other related metal topologies, and this enhancement is related to the encapsulated metal’s morphology (aspect-ratio). Applications of this particular metal topology in to biological systems are currently under investigation in the PI’s laboratory.

The second area of investigation under the support from ARO was in regards to the nonlinear optical properties of particular branched organic molecules. From both nonlinear absorption and degenerate four-wave-mixing measurements we found that the nonlinear optical activity of a branching chromophore architecture was significantly enhanced in comparison to linear analogs of similar chromophore number density. A number of branching chromophore systems were utilized to test this hypothesis and the results from the PI's group as well as a number of recent reports have brought this approach to the enthusiastic interests of this research area. In order to understand the mechanism of the nonlinear optical enhancement process, the PI's group has carried out detailed time-resolved spectroscopic measurements to probe the excited and relaxed properties of the branched molecules. From both time-resolved fluorescence anisotropy and transient absorption anisotropy measurements for particular branched structures it was found that the initial (first ~100 fs) of the excited state is delocalized. This suggests that for branched systems with significant charge-transfer character for each of the participating chromophores the excitation initially goes through an intermediate state, which is delocalized before the charge transfer process stabilizes by localization on one of the chromophores in the branching structure. This implies that the enhanced nonlinear optical property is related to the strong intramolecular interaction between chromophores. The PI has taken this investigation further by probing this “intermediate state” by three-pulse-photon-echo (3PEPS) measurements. Here, a significantly different
 photon-echo decay profile was obtained with the branching structure as compared to linear chromophore analog which was the building block of the branched structure. These results are the first of their kind, which utilize this very sensitive technique to probe related parameters such as reorganization energy, electronic and nuclear coupling to the both or solvent, as well as inhomogeneous broadening in structural disordered organic chromophoric media.

The third area of research that has been supported by APO under a young investigator award regards the quantum optical properties of optical macromolecules. Through this investigation, we found that it is possible to generated squeezed states of light in organic macromolecular materials. The mechanism of producing photon-number squeezed states of light was by multi-photon absorption in dipolar organic macromolecules. This was important, as this investigation introduced particular organic materials into the important field of quantum optics which may have applications in all-optical signal processing as well as in understanding new phenomena with correlated photon statistics. The PI's group has extended these studies with investigations of entangled photon-statistics. Measurements of biphoton absorption in organic macromolecules may lead to new applications regarding the detection of chemical and biological agents with optical methods only requiring a small number of correlated photon pairs.

Below is a more detailed account of our findings.

A) Nonlinear Transmission Measurements in Novel Branched Macromolecules

From our measurements and reports under this ARO supported project we have found that different metal topologies show good optical limiting behavior where in some cases a morphology dependent effect was observed. Our first report of the nonlinear optical properties of these novel nanocomposites was investigated with 6.5 ns laser pulses at 532 nm. The result of the nonlinear transmission measurement is shown in figure 1.
Figure 1: The nonlinear transmission result for silver dendrimer metal nanocomposites at 532 nm.

When the input fluence varies from 0.7 to 10.0 J/cm² (equivalent to the increase of the peak irradiance from 0.2 to 1.3 GW/cm²) the transmission decreases by 62%. The threshold fluence for optical limiting is around 2.0 J/cm². The optical limiting performance of the silver dendrimer nanocomposites compares well to the results obtained with novel organic structures. Through further detailed measurements the PI’s research group has established the strong NLO properties of certain dendrimer nanocomposites.

Further measurements with gold dendrimer nanocomposites and gold nanosphere and nanorods also proved to be important in understanding the nonlinear transmission and optical limiting properties of metal topologies. Synthetic procedures were carried out to probe the NLO properties in gold dendrimer nanocomposites with similar metal content as compared to the silver dendrimer nanocomposites. In collaboration with El-Sayed (Georgia Inst. of Tech.) samples of gold nanospheres and nanorods were also carried out keeping the metal content constant or similar to what was observed for the dendrimer metal nanocomposites. Also, further synthesis by the PI’s group was carried out to probe the NLO properties of chromophore functionalized dendrimer metal nanocomposites. What was observed from these measurements was that the functionalized dendrimer metal nanocomposite system showed the strongest NLO effect and it was significantly larger than the result of metal nanosphere or nanorods with similar metal content. This gave a strong indication that the NLO process of nonlinear transmission in the functionalized dendrimer metal nanocomposites was significantly different that observed for the pristine metal topologies (with miscelles).
Figure 2: Nonlinear transmission results for a comparison of different metal topologies as well as dendrimer metal nanocomposite morphologies. Both gold nanorods and nanospheres were measured (at 532 nm, ns pulses) as well as gold dendrimer nanocomposites and a functionalized chromophore dendrimer metal nanocomposite. The results suggest that while the mechanism of the nonlinear transmission effect in these systems does involve the metal nanoparticle, this effect is enhanced by the dendrimer architecture as well as in the functionalized chromophore.

We have also investigated the mechanism of the nonlinear transmission properties in dendrimer nanocomposites. Due to the complexity of the metal particle morphology, there has not been a completely self-consistent mechanism that could explain the results obtained from all dendrimer nanocomposite architectures. There are, however, important characteristics that may give a plausible explanation for the mechanism which is related to a nonlinear scattering mechanism. Similar effects of nonlinear light scattering have already been reported with other metal nano-structures. For example, Sun and coworkers suggested that the optical limiting properties observed in silver nanoparticles could be associated with transient scattering processes that are attributed to photothermal processes. Here, the strong light scattering processes serve to diffuse the intensity of the input beam to very low (tolerable) levels. However, as in the case of the size-dependent optical limiting effects observed by Mostafavi et. al., these processes are relatively slow in comparison to intrinsic optical excitations in the metal spheres and rods.
B. New Synthesis and Measurements with Dendrimer Nanocomposites

Our investigations of the optical properties of novel organic-inorganic hybrid materials continued with new synthetic strategies for development of better dendrimer metal nanocomposite materials. This was followed by very detailed photo-physical characterization of these materials. For example, new gold dendrimer metal nanocomposites of different morphology were synthesized and investigated by the PI’s laboratory. The synthesis of a dansylated (NLO chromophore system) functionalized dendrimer metal nanocomposite was carried out. The results of the nonlinear transmission measurements suggested an enhancement for the chromophore functionalized dendrimer nanocomposite system.

Figure 3: The nonlinear transmission of a dendrimer functionalized with a NLO chromophore (dansyl) and a dendrimer metal nanocomposite system with a functionalized chromophore. The result suggests that the chromophores contribution to the NLO effect can be enhanced by addition of metal nanoparticles.

Another morphology containing hydroxy terminated PAMAM G5 was used as a template to stabilize the gold nanoparticles as well. A self-reduction reaction and exchange of Cu nanoparticles were proposed for this synthesis of dendrimer-gold nanocomposites and this work suggested that it was possible to encapsulate a single small metal particle inside each branching dendrimer architecture. In general, our results in this area concluded the point that enhanced NLO properties of gold nanoparticle materials not only depend on the geometry of the metal nanoparticles, but also on the templates used to form the nanocomposites. We will continue further studies in this area, with new metal nanocomposite topologies and putting the samples in the solid state.
C. Mechanism of Emission in Small Metal Nanocomposites

Investigations of the mechanism of emission in metal nanoparticles as well as the process of enhancement were also carried out. Our studies focused on dendrimer metal nanocomposites as well as metal nanospheres and nanorods in this respect. In particular, our results give important information regarding the characterization of ultra-fast emission in metal nanorods and nanospheres. We had first observed ultra-fast emission in gold dendrimer metal nanocomposites and found that the decay was very fast with a highly depolarized character. We also found that the mechanism of emission of such small metal nanoparticles was not well established at that point. This gave greater enthusiasm to look at more general metal topologies in order to characterize what was happening with the dendrimer metal nanocomposites. These studies also concern a fundamental question involving the mechanism of emission in metal particles. As it is already known, there are two possible mechanisms for the ultra-fast emission from gold nanoparticles (emission from the surface plasmon resonance (SPR) and/or emission due to band-to-band transition (d→sp conduction band).

![Fluorescence intensity vs. time graph]

**Figure 4:** The dynamics of the emission decay measured by fluorescence upconversion spectroscopy. The decay curve suggested that the principle emission is a fast component on the order of ~80 fs and a slower component (several ps). We have attributed the fast component to the emission of the metal nanoparticles in the dendrimer host.

The results of the measurements give a strong suggestion that the emission is primarily from band-to-band transitions. The fabrication of the metal (gold) nanorods was accomplished in collaboration with Professor M. El-Sayed of Georgia Tech University in the Department of Chemistry. From measurement of the ultra-fast emission amplitude as a function of wavelength we compared the
results of different aspect ratio metal particles. We found a very strong enhancement in the longitudinal resonance for the case of the metal nanorods. Actually, in these measurements the results of the rods was normalized against those of the metal nanospheres which was not expected to have a significantly larger value at longer (longitudinal) wavelengths. These measurements strongly suggested that the emission was mainly a result of intra-band transitions in the metal nanoparticles. These studies suggest that the metal geometry does play a role in the nonlinear absorption of the metal particles.

**Figure 5:** The calculated and measured values of the enhanced (relative to metal nanospheres) emission from two different metal nanorod samples of different aspect ratio. It is obvious from these results that most of the enhancement is in the longitudinal resonance, where the longer metal nanorods are expected to have larger contributions from local field enhancement processes.

**D. Quantum Optical Effects in Novel Organic NLO materials**

Under support of the ARO we have also investigated the quantum optical effects in organic NLO materials. For example, we have shown that certain nonlinear optical polymers and chromophores with large nonlinear coefficients could be used for the generation of photon-number squeezed states of light.\(^{51}\) We also have demonstrated the reduction of photon-number fluctuations below the shot-noise level (photon-number squeezing) by two-photon absorption in an inorganic semiconductor material consisting of a thin film of TOPO-decorated CdSe nanocrystals embedded in a PMMA polymer host. The photon-number squeezing was measured at 800 nm, where the linear absorption of the material was negligible. The amount of photon-number squeezing from the CdSe system was \(_5\)\% for a moderate value of nonlinear transmission. This observation was
possible due to the large nonlinear absorption exhibited by the system of CdSe NCs embedded in PMMA and also due to the reduced linear scattering losses in thin films. The CdSe squeezing data was compared to results previously obtained for the first time in a nonlinear optical polymeric material by the PI's laboratory under support from ARO.

\[ F = \frac{\text{[laser noise – electronic noise level]}}{\text{[shot-noise – electronic noise level]}} \]

@ 10.5 MHz
Sample: R-478 thin film
800 nm; 100 fs pulses

Figure 6: The first measurements of the generation of squeezed states of light in organic material. The amount of squeezed light (lowering of the fano factor) is significant in comparison to what has been observed for inorganic crystals as well as for other vapor experiments where the interaction length was several orders of magnitude longer than what was used in the thin film polymeric sample.

The achievement of photon-number squeezing in these novel materials gives the opportunity for future application in the improvement of the signal-to-noise ratio in optical communications. The magnitude of the squeezing observed was comparable to other inorganic and atomic vapor results, even though the interaction length in the thin film of the polymeric material was more than three orders of magnitude smaller than in the inorganic crystal systems.
We are most grateful for the Army Research Office for support of this program at an early time in the PI’s independent career. Under this support there have been postdoctoral assistants, graduate students, undergraduates as well as high school student that has participated in the research. The names are listed below are the scientists participating in this program have moved on toward developing further their careers in science and engineering as well as on to other professional schools.

Postdoctoral Assistants
Dr. Radu Ispasiou, now at Gemfire Inc. (California)
Dr. Ying Wang, now a postdoctoral fellow in the PI’s laboratory
Dr. X. Xie, now a postdoctoral fellow in mechanical engineering

Graduate Students
Mr. Sridhar Lahankan, now a fourth year graduate student
Ms. J. Yan, now a graduate student in computer science, received MS degree

Undergraduate Students
Mr. Richard West, Now a medical student at Ohio State University
Ms. Nicole Dolney, Now an engineering student at U of Michigan

High School Students
Mr. Mark Fleming, accepted to Georgetown University and should start there next fall

Publications in Refereed Journals


HONORS AND AWARDS

03/03 Wayne State University Career Development Award
02/03 Lloyd Ferguson Young Scientist Award (NOBCCHE)
02/03 Alfred P. Sloan Foundation Fellow
05/02 The Camille and Henry Dreyfus Foundation Teacher-Scholar Award
01/02 National Science Foundation CAREER Award
04/01 College of Science Teaching Award, Wayne State University
09/00 Army Research Office Young Investigator Award
04/00 Burroughs Welcome Fund Travel Award
09/97 National Research Council Ford Postdoctoral Fellowship, University of Oxford, Oxford, UK

Invited papers presented at meetings


Approaches To Combat Terrorism, Washington DC, Intelligence Community and National Science Foundation Workshop, Nov. 2002.


Society of Physicists and Optical Engineers and Instrumentation Conference (SPIE), Committee Director of Metal Nanostructured Materials Program, July, 2002.

National meeting of Black Chemist and Chemical Engineers (NOBCCHE) Invited speaker at symposium held by Rohm and Haas Inc. “Organic Macromolecular Optical Applications,” March, 2002


Invited talks at other institutions


Purdue University, “Ultra-fast Investigations of Energy Transfer in Organic Dendrimers,” April, 2002.


Oakland University, Department of Physics, "Nonlinear Optical and Time-Resolved Properties of Dendrimers and Dendrimer Metal Nanocomposites," Nov. 2000.

