

CHARACTERIZATION OF SILVER NANOPARTICLE PLASMON EFFECTS ON SYSTEMS OF FREE AND BOUND CHROMOPHORES, William R. D. Boyd, Wojciech Haske, Michal Malicki, Matteo Cozzuol, Matthew M. Sartin, Joseph W. Perry\*, Georgia Institute of Technology, Department of Chemistry and Biochemistry, Atlanta, GA 30332, [joe.perry@chemistry.gatech.edu](mailto:joe.perry@chemistry.gatech.edu)

Silver nanoparticles (AgNPs) are at the forefront of research for applications such as optical power limiting and biosensor technology. AgNPs exhibit plasmon resonance; that is, they are highly polarizable and in the presence of an incident electromagnetic field at resonance frequency their electrons oscillate and produce a resultant localized electric field that is greater than solely that of the incident light. Synthesis of ligand-coated AgNPs was performed and the AgNP size distribution and average diameter were determined by Transmission Electron Microscopy (TEM) and analysis using ImageJ software. Thiolated chromophores 4,4' bis (N-phenyl, N-3-methylphenyl amino)biphenyl (TPD), and 1,4-bis(4-nitrostyryl)2-methoxy-benzene (BN) were attached to the ligand-coated AgNPs by a ligand-exchange reaction. The stability of the chromophore-coated AgNPs was studied using time-based fluorimetry and UV-vis spectroscopy. Stability measurements determined a 5:1 mixture of toluene/DMF to be the best solvent for TPD-coated AgNPs, and dichlorobenzene the best solvent for BN-coated AgNPs. Modeling of the effects of AgNP plasmon resonance on the excited state decay rates of the bound chromophores was performed in accordance with the theory derived by Gersten and Nitzan for excited state molecules near spheroids. The results predict enhancements for the radiative decay rates of the chromophores oriented perpendicular to the AgNP surface, and a suppression of the radiative decay rates of the chromophores oriented parallel to the surface. For both orientations, the non-radiative decay rate is calculated to be greater than that of free chromophores, resulting in a significant reduction of the fluorescence quantum yield predicted for the bound chromophores. The strongest effects of plasmon resonance on the radiative and non-radiative decay constants were predicted for chromophores with fluorescence emission near that of the AgNP plasmon resonance absorption peak at ~430 nm. The theoretical results were explored by experimental probing of the fluorescence lifetimes of both free and bound TPD and BN. Fluorescence lifetimes were measured using Time-Correlated Single Photon Counting (TC/SPC). Little if any effect from plasmon resonance on the bi-exponential fluorescence decay of BN could be resolved. Alternatively, the tri-exponential fluorescent decay of TPD-coated AgNPs contrasted with the mono-exponential decay of the free TPD. An investigation of the shortest lifetime component for the TPD-coated AgNPs revealed it to be remarkably close to the lifetime predicted for TPD oriented perpendicular to the AgNP surface. Further research is ongoing to resolve the processes behind the measured tri-exponential fluorescence decay of the bound TPD and to confirm whether the short lifetime component is indeed that of bound TPD.

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