Title:	Modulating Photophysical Properties of Dye-Loaded Gold Nanoparticles Through Plasmon-Molecule Coupling
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Keywords:	Photophysical Gold Nanoparticles
Issue Date:	Aug-2022
Publisher:	IISER Mohali
Abstract:	Metal nanoparticles (MNPs) exhibiting surface plasmon resonance (SPR) properties can interact with the oscillating dipoles of organic molecules in a pronounced manner. Molecules which absorb light near to the SPR absorption peak of MNPs can induce changes in the photophysical and electronic properties of MNPs due to plasmon-molecule interactions. These interactions can also increase or decrease the field incident on the dye molecule and perturb their electronic transitions. Plasmon-molecule interactions are governed by several factors such as the spectral overlap between the molecular and plasmonic resonance, chemical composition and concentration of the dye molecule, shape and size of MNPs and the distance between MNPs and dye molecule. If the coupling interactions are weak, various surface- enhanced phenomena are known to arise whereas strong coupling often results in the formation of hybrid ‘plexcitonic’ states. Irrespective of the strength of the coupling interactions, the optical properties of the hybrid systems are markedly different from those of their constituents. Page 1 of 3Plasmon-molecule coupled systems have incredible potential in materials science and biology. Several literature reports exemplify their utility as ultrafast switches, bistable devices, modulators, sensors, photocatalysts and biological imaging agents. A limited number of examples are also known wherein molecule-plasmon interactions have been utilized in photodynamic therapy (PDT) although the mechanistic details of such systems are generally overlooked. Motivated by these facts, we aim to study systematically the photophysical properties of a series of nanocomposites with the objective of understanding the underlying mechanism of plasmon-molecule interactions. We chose gold nanoparticles and organoboron compounds for our investigations because of the low toxicity and tuneable absorption profile of gold nanoparticles and the luminescence features of the dye molecules. Chapter 1 focuses on literature review of plasmon-molecule interactions from fundamentals to applications. We have briefly discussed surface plasmons, excitons, and their interactions in terms of coupling strength. Further, various types of plasmon-molecule coupled systems and their applications have been discussed. Finally, the recent advancements in plasmon-molecule interactions for applications in PDT have been discussed, highlighting the importance of mechanism which will help in the development of new plasmon-molecule coupled systems. Chapter 2 describes the synthesis and characterization of dye molecules as well as their nanocomposites. NMR spectroscopy revealed that various supramolecular interactions between the individual components play a key role in the formation of stable nanocomposites. We studied the effect of structural variations in the dye molecules B1-B5 on nanocomposite formation and it was observed that sterically bulky molecule destabilizes the nanocomposites. Further, the dye molecule B6 containing a stimuli-responsive group was employed so as to study the effect of immediate environment on the photophysical properties. We also synthesized a multi-chromophoric nanocomposite containing two dye molecules in order to study the impact of interaction between the two molecules on the photophysics of the nanocomposites. Chapter 3 discusses the photophysical properties of all the nanocomposites. The nanocomposite formation resulted in major changes in the photophysical properties of their components: bathochromic shifts were observed in the absorption maxima of the dye molecules and gold nanoparticles whereas the fluorescence of the dye molecules was completely quenched. On the other hand, in the multi-chromophoric nanocomposite, Förster resonance energy transfer (FRET) was observed to occur between the two dye molecules on the surface of gold nanoparticles. This opened up radiative pathways and made this nanocomposite Page 2 of 3moderately fluorescent. In the case of the dye B6 wherein the absorption overlap was minimal with gold nanoparticles but a significant overlap was observed between the fluorescence of B6 and the absorption of gold nanoparticles, plasmon-enhanced luminescence was observed. Further, we observed that chemical structure of dye molecules had a significant effect on the photostability and photosensitization properties of the nanocomposites. Thus, our findings highlight the importance of spectral overlap between dye molecule and gold nanoparticles on plasmon-molecule coupling. Chapter 4 focuses on the potential application of the synthesized nanocomposites as photosensitizers for PDT. Ultrafast spectroscopy was used to map the excited state processes in the nanocomposites and our investigations revealed hot electron migration from dyes B1-B3 to gold nanoparticles. Further, the nanocomposites exhibited enhanced plasmonic lifetimes which resulted in an increase in singlet oxygen generation upon plasmonic photoexcitation. However, we observed a reversal in the direction of hot electron migration from gold nanoparticle to dye molecule B6 which resulted in enhanced luminescence. Further, the nanocomposites were found to be photostable and biocompatible and thus were utilized as photocytotoxic agents against cancer cells and luminescence imaging agents.
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