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On the fluorescence properties of chromophores near metallic nanostructures

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Summary

Nanostructures of noble metal (copper, silver, gold, etc.) can influence the photophysical properties of nearby molecules, because of the interaction of the so-called surface plasmon resonance of the metal nanostructure with the molecular transition dipole. The surface plasmon resonance, loosely defined as collective excitation of the free electrons within the metal nanostructure, has an effect on the local electromagnetic field up to hundreds of nanometres, which in turn is ‘felt’ by a molecule in close proximity of the nanostructure. Consequently, the fluorescence intensity of such a molecule is increased (enhancement) or weakened (quenching). In this Thesis, the fluorescence of chromophores which are chemically connected to metal nanoparticles is investigated. Chapter 1 explains the concept of metal enhanced fluorescence and gives examples of quenching and enhancement of the fluorescence of chromophores found in literature.

In the research described in the Thesis, chromophores were placed in the vicinity of gold nanoparticles (AuNPs) via a disulfide group, which can bind to the surface of the nanoparticle. The results of these studies are discussed in Chapters 2 and 3. For this purpose, two different chromophores were synthesised. A perylene monoimide based chromophore that was connected to a disulfide group via a tetraethylene glycol alkyl chain (PMIdS) is described in Chapter 2. A 4-amino substituted naphthalimide derivative was connected to a cyclic disulfide moiety which stems from thiocyst acid (TNI) as described in Chapter 3. Thereafter, AuNPs were functionalised with these novel molecules after which changes in the fluorescence from the chromophores were examined. According to quantum chemical calculations strong quenching of fluorescence of both the chromophores should take place following binding with AuNPs as a result of efficient excitation energy transfer from the dye to the particle. Factors such as the size of the metal nanoparticles, distance of the chromophore from the surface, and the relative orientation are important variables in the extent of quenching or enhancement of the fluorescence. In a longitudinal orientation, fluorescence enhancement may take place, whereas in a perpendicular alignment only quenching is predicted as in that case there is no co-linearity between the transition moment of the chromophore and the AuNP-induced dipole. The binding of disulfides to AuNPs was investigated using fluorimetric titration experiments, in which unfunctionalised AuNPs are added to a solution of the chromophore. Indeed, strong quenching of the fluorescence is observed. Using two different types of disulfide linker, the binding efficiency to gold nanoparticles could be compared. It was found for the linear disulfide that under the used conditions their affinity for the gold surfaces is smaller than usually presumed and complexation of the disulfide leads to an equilibrium (association constant \( K = 5 \times 10^5 \text{ M}^{-1} \)) instead. Desorption of the chromophore from the surface of the nanoparticles at low concentrations is confirmed using...
fluorescence correlation spectroscopy; the appearance of free PMIdS ligands from a purified sample of fully functionalised AuNPs was observed over a period of several days. By this means, the fluorescence lifetimes of ‘bound’ and ‘free’ chromophores could be determined. In accordance with the predictions, the fluorescence lifetime of the bound chromophore was much shorter than that of the free chromophore and the extent of quenching was estimated at 95%, which is not incompatible with the theoretical prediction. In contrast, the cyclic disulfide in TNi binds more strongly to the metal nanoparticles since in this case two gold sulfur bonds are formed, and desorption from the surface is less likely to occur. In this case, the fluorescence of the total mixture is reduced to 23%. The remaining fluorescence is assigned to unbound chromophore in the solution. In a competition experiment, using both TNi and PMIdS, the fluorescence of TNi decreases faster than that of PMIdS; this confirms that the two types of disulfides have different binding efficiencies with the gold surface. Studies on TNi also revealed biexponential fluorescence decay. The short component is tentatively assigned to the result of intramolecular photoinduced electron transfer from the disulfide group to the naphthalamide moiety. This process is more pronounced in non-polar solvent, since the aliphatic chain can fold by, for example, forming intramolecular hydrogen bonds, and in this folded conformation these two parts are closer together than in an extended conformation which explains the biexponential decay because of conformational heterogeneity.

In Chapter 4 facile syntheses of derivatives of perylene monoimides (PMI) and perylene diimides (PDI) bearing reactive carboxylic acid groups are described. The functional group can be used to incorporate these chromophores into multifunctional molecular systems. In addition, a novel method has been found to prepare asymmetric N,N'-substituted PDI derivatives. The photophysics of these compounds was studied and it was found that the inclusion of a functional group on the imide site does not have an effect on the properties of the chromophore. Therefore, the parent PMI and PDI derivatives could still be used as model chromophores. Substitution on the 9-position of PMI derivatives with an electron-rich group results in push-pull systems with solvatochromic absorption and fluorescence. Two PMI derivatives bearing an alkoxy group on this position were prepared and studied. Conveniently, this type of molecule can readily be incorporated as an environment-sensitive fluorescent probe. Using photodegradation experiments, their photostability was evaluated and it was found that this type of compound is sufficiently photostable against high laser powers and they are good candidates to be used as probe in confocal imaging and even for single molecule detection.

Other chromophores that can be employed in research towards fluorescence enhancement by metal nanoparticles are considered. Weakly fluorescent chromophores may more likely encounter metal-enhanced fluorescence, since the metal nanoparticles could strongly enhance the radiative decay rate and the rate of absorption, whereas the effect of metal nanoparticles may only be limited on strong fluorescent molecules because the fluorescence quantum yield is already high. Di-aryl
substituted 1,2,4,5-tetrazine derivatives, which are studied in Chapter 5, have a low fluorescence quantum yield and their absorption bands have good overlap with the surface plasmon band of gold nanoparticles. In this Chapter, we focus on the photophysical behaviour of this type of chromophore. The predicted transitions from the TD-DFT calculations correspond well with the experimental absorption spectra. The electronic transitions could be assigned on the basis of these TD-DFT calculations. Excitation to the first excited state results in weak fluorescence ($\Phi_f \approx 10^{-4} - 10^{-3}$). Interestingly, fluorescence from a higher excited state is found upon excitation to a higher energy state. Time-correlated single photon counting (TC-SPC) and femtosecond transient absorption (fs-TA) measurements were carried out to elucidate the fast processes after excitation to the $S_n$ state. These measurements showed that internal conversion from the $S_n$ state to the first excited $S_1$ state is on time scales of 20 - 30 ps. It is postulated that this process is so remarkably slow because of the large energy gap between the two states, despite the fact that several other states exists between them. This slow internal conversion explains the presence of higher excited state emission since direct emission can thus compete with this process leading to observable emission for a higher excited state.

Instead of studying the fluorescence of chromophores in solution, confocal microscopy was employed as a useful tool in a search for local ‘hot spots’. In Chapter 6, an array of gold nanodots was deposited on a glass coverslip via gold evaporation in a thermal evaporator under vacuum conditions through a nanostencil which was thereafter functionalised with a perylene monoimide derivative. This way, it would have been possible to find exact positions where the fluorescence is enhanced, for example, when the chromophore is sandwiched between two gold dots. When a spacer consisting of a polystyrene film is spincoated between the gold pattern and the chromophore, no evidence of quenching or enhancement of the fluorescence is found. However, when the chromophore layer is directly on top of the gold pattern, the fluorescence is completely quenched. On the regular pattern, the Au layer is even too thick to be transparent for light to pass through, and it shields the excitation light and emission of the chromophore. During the preparation of the regular gold pattern by shadow mask evaporation through a nanostencil, the gold atoms could diffuse and which resulted in a halo of a thin transparent continuous Au layer on the surface.