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Subject: Scientific review of the thesis manuscript submitted by Marta Gordel and entitled "Synthesis, optical studies and functionalization of plasmonic nanoparticles for biological applications"

The thesis project of Marta Gordel, jointly supervised by Professor Marek Samoc in Wroclaw and Professor Malcolm Buckle in Cachan, deals with the design and optical properties of hybrid nanostructures associating gold particles and a wide variety of organic or biochemical molecules. In particular, the author focuses on the use of gold nanorods as optical contrast agents or sensors for biomedical applications. Through this extensive experimental study, Mrs. Gordel demonstrates the wide variety of skills she has applied and developed to produce and analyze these complex samples. It is important to stress that the author has performed experimental studies in scientific fields as varied as nanoparticle synthesis, characterization and purification; surface chemistry and optimization; linear and nonlinear optical spectroscopies as well as cellular functionalization and imaging. This considerable work has led to a number of peer-reviewed publications, where Mrs. Gordel is often the first contributing author.

The thesis manuscript is organized in 6 chapters. The first chapter reviews the main theoretical background, in the design and optical properties of gold nanostructures, required to understand and analyze the experimental data of the thesis. The second chapter gives an overview of the experimental techniques used throughout the manuscript. While not providing novel data, these two chapters are essential for the clarity of the manuscript and demonstrate the thorough knowledge of the author in the numerous fields developed in the thesis.

Chapter 3 introduces novel, and yet simple, physicochemical techniques to purify and assemble gold nanorods. In particular, the author demonstrates how a simple glucose gradient allows the separation of the desired nanostructure (gold nanorods) from undesired byproducts. Furthermore, using a layer-by-layer surface chemistry approach, she produces assemblies of end-to-end assembled gold nanorods that exhibit large field enhancements (with potential applications in surface enhanced spectroscopy). A conjunction of spectroscopy, electron microscopy and numerical simulations allow Mrs. Gordel to fully characterize these architectures, even though a discussion on the typical interparticle distances and their influence on the optical properties would have been welcome.

Chapter 4 is an original study of the stability of gold nanorods under high optical excitation. This is an important study for the applicability of such nanostructures as contrast agents in nonlinear optical microscopy where high photon fluxes are employed. The author shows nicely the behavior of gold nanorods and the influence of different stabilizing surface chemistries. The ability to influence specific nanorod subpopulations and perform a "spectral hole burning" in the extinction spectrum is particularly original.

Chapter 5 deals with the third-order nonlinear properties of gold nanoshells and gold nanorods, studied using the z-scan technique. The author shows nicely that these properties are dominated by one-photon saturation effects and that, thanks to their weak optical scattering, gold nanorods exhibit superior nonlinear refraction than nanoshells. It would have been interesting to propose new design routes for more efficient two-photon absorbers. The chapter also deals with the nonlinear properties of novel organic dyes. While this original work led to several publications, I believe this already dense manuscript would have been clearer if this part, that does not involve gold nanostructures, had been excluded.

The last chapter of the thesis focuses on DNA-functionalized gold nanorods as sensors and optical contrast agents. This part further demonstrates the wide array of experimental techniques developed in this thesis, going all the way to imaging of the produced nanostructures in live cells. In particular, the thorough analysis of the number of DNA strands attached per particle is compelling.
The author introduces DNA strands with organic dyes to use as sensors or enhanced fluorescent markers. She demonstrates a modest fluorescence enhancement of ~2 but nicely demonstrates how its distance dependence can be used for sensing (even though the concentration sensitivity of the sensor is not discussed). She also shows the uptake of these functionalized particles in cells where the distance-dependent enhancement is preserved and can be observed in confocal microscopy. This final part of the manuscript could be improved by a comparative discussion with published results from the literature.

Overall, this manuscript describes an extensive body of novel and original experimental research that spans several fields of science. Furthermore, it is important to note that this thesis was conducted between two countries and between chemistry and biology departments in a field requiring a strong background in physics. This indicates again the large scientific culture of Marta Gordel. For all these reasons, and based on the quality of the described results, I recommend that the candidate can be admitted to the defense of the thesis.

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