UNIVERSITY OF JYVÄSKYLÄ
Department of Chemistry

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To the Faculty of Chemistry, Wroclaw University of Science and Technology

Review of the doctoral thesis of Magdalena Waszkielewicz

The PhD thesis of Magdalena Waszkielewicz deals with ligand-protected gold nanoclusters and their spectroscopic properties, in particular nonlinear optical properties. The thesis is a monograph with 167 pages and 322 references. It is based on 5 original papers which are published in high quality journals. Waszkielewicz is the first author in one of them, second author in three of them and the third author in one of them. Additionally, she is an author of one more paper which does not deal with gold nanoclusters. The thesis constitutes a coherent entity.

The first part of the thesis, which covers roughly one third of the total, is a review of relevant literature. It starts with the statement of motivation and aims. The main driving force of the work has been to study nonlinear optical properties of metal nanoclusters. The topic is very relevant as there is only very limited amount of information on nonlinear optical properties of metal nanoclusters. The literature review goes through the synthesis methods and basic chemical properties of mainly gold nanoclusters. Then it proceeds to linear optical properties and in this context electronic structure of gold nanoclusters is discussed. Chirality is handled after which nonlinear optical properties are discussed including some results on bioimaging using gold nanoclusters as contrast agents. The literature review part is logical and well written, it includes all the relevant topics of the thesis and it is based on good knowledge on literature. It gives a nice overview of the field of the thesis.

The experimental section starts with a description of synthesis, purification and characterization protocols of the thesis. Many different samples have been studied including small clusters with Au_{18} and Au_{25} cores and various ligands, aggregates of small clusters, silver-doped gold nanoclusters and silica-coated gold nanoparticles. Thus, the range of particles is quite broad and it has required a lot of work to develop all the protocols and characterization procedures, even though they are based on previously published work. Thus, it can be concluded that the candidate has gained extensive experience in synthesis and characterization of metal nanoclusters and nanoparticles. There is one result that raises questions. In section 2.1.3, for example, TEM analysis yields the average diameter of 2.16 nm for $Au_{18}(SG)_{14}$ clusters. This value seems too high for such a small cluster. Perhaps the particles visible in TEM are small aggregates. Some more discussion on the TEM analysis and the diameters would have been useful.

The next section deals with linear optical properties, mainly absorption and emission spectra. The candidate has also determined fluorescence quantum yields for various clusters and studied the effect of pH on the spectral properties. Several interesting results have been obtained such as enhancement of fluorescence at low pH and transformation of the $Au_{25}(Capt)_{18}$ cluster to

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$Au_{23}(Capt)_{17}$ cluster, which shows bright fluorescence. These results show that the clusters are dynamic species and they evolve according to the environmental conditions.

Next section deals with formation of aggregates from mixed AgAu clusters. It is shown that large spherical aggregates form spontaneously and the size and distribution of the aggregates depend on Ag:Au ratio and pH. Additionally, polymers were used to stabilize the aggregates. Optical properties were studied and the main conclusion was that the aggregation had little effect on them indicating that there is no significant inter-cluster interaction at the electronic structure level. The study gives a good basis for tailoring sizes of the aggregates which may turn out to be useful in future applications. In this section, enhancement of emission and spectral shift was observed in some instances but it is not clear if these effects are solely due to increased scattering leading to longer effective optical path or if some other effects are also responsible for the observations.

The last part of the thesis handles nonlinear optical properties of metal clusters. The main technique used to measure the properties, the z-scan method, is introduced and explained. Several clusters are characterized by the z-scan method yielding, via analysis of the data, nonlinear cross sections for wide spectral range. This is very useful and new information as previously only a few wavelengths have been measured for some clusters. The cross-sections are very large promising applications in optical limiting and two-photon imaging. Thus, the data presented in the thesis is of high importance for understanding the nonlinear optical properties of metal nanoclusters. The data also constitutes an important basis for possible applications exploiting nonlinear properties of nanoclusters. A novel contribution is made by performing chiral z-scan measurements. These measurements yield two-photon circular dichroism spectra. It is found that the nonlinear circular dichroism is about two orders of magnitude higher than the linear one, which is promising for further development.

Finally, two-photon induced fluorescence was applied to biological samples for imaging. The results are quite encouraging for further development of bioimaging based on metal nanoclusters.

Overall, the thesis by Magdalena Waszkielewicz is a coherent study of metal nanoclusters. Although the main focus is in nonlinear optical properties many new and interesting results were obtained also regarding their synthesis, chemical properties and linear optical properties. I am impressed by the extent of the work. The candidate has learned a wide range of methods from wet chemistry to nanocharacterization and further to laser technology and she was able to carry out a complete study of metal nanoclusters starting from synthesis and proceeding all the way to bioimaging. The experiments are carefully conducted and the results are relevant and important. The work is well written and forms a logical entity.

In summary, in my opinion, the thesis fulfills the requirements for receiving the PhD in materials engineering. In addition, for the reasons detailed above, I recommend that the work is awarded with distinction.

I am happy to answer any questions you might have.

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Sincerely yours,

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