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# ОТЗЫВ

члена диссертационного совета Светлана Анатольевна Сантер (Svetlana Anatolyevna Santer) на диссертацию Сыча Томаша Сергеевича на тему «Люминесцентные кластеры благородных металлов, стабилизированные белковыми матрицами: фотофизические и структурные свойства, практические применения», представленную на соискание ученой степени кандидата физико-математических наук по специальности 1.3.8. Физика конденсированного состояния.

In this study, Mr. Sych explores two families of protein- and amino acid stabilized clusters: silver- and gold- based. Tomash's dissertation presents a systematic investigation of such clusters, including a full-scale study of the spectral and structural properties of the complexes. The study includes the optimization of synthesis conditions through varying reagent concentrations and external conditions, determination of photophysical and structural properties of the clusters, and exploration of their potential analytical applications. The samples were synthesized using wet chemistry methods, and their spectral properties were determined using stationary fluorescence and absorption spectroscopy. The study also used time-correlated single photon counting to determine the lifetime of the clusters' fluorescence, and a combined approach of Raman spectroscopy, X-ray photoelectron spectroscopy, high-performance liquid chromatography, and quantum chemical calculation to determine their structural properties.

The work consists of 5 chapters: first, a comprehensive introduction and literature review on the current state-of-the-art of production, properties, and practical applications of luminescent metal clusters (namely, silver and gold) is given, followed by a more detailed look at the methods of qualitative and quantitative detection of blood serum components using fluorescent clusters. This provides a solid basis for the main issues outlined in the thesis.

In Chapter 2, Mr. Sych explains the methodological aspect of the work, discusses the synthesis strategies and their optimization for obtaining silver and gold luminescent clusters stabilized with different amino acids and proteins. The main difference between the two is that to synthesize silver-based clusters, the presence of a reductant is necessary, while in the case of

gold, the reduction is driven by the presence of amino acid residues. In the second part of the chapter, Tomash provides a theoretical basis for the characterization methods used in his research, including, but not limited to Raman and X-ray photoelectron spectroscopy, high performance liquid chromatography, fluorescence and absorption spectroscopy.

Chapter 3 and 4 are devoted to the results and discussion of the synthesis and characterization of silver and gold clusters stabilized by protein and amino acid matrices, respectively. The third chapter of Sych's work discusses the influence of protein matrix concentration on the formation of silver fluorescent clusters. Lower matrix concentrations are found to be preferable for determining spectral characteristics in the UV range due to reduced protein absorption. Optimal synthesis conditions for low-concentration matrix stabilized clusters are investigated, with cysteine and tyrosine amino acid residues found to be involved in the binding of the clusters to the matrix. The structures of the investigated complexes are also proposed: the silver cluster stabilized by serum albumin contains five silver atoms, while the tyrosine-stabilized cluster has a triangular geometry and is stabilized by three molecules of tyrosine in a special semiquinone form.

Chapter 4 focuses on the synthesis and characterization of fluorescent gold clusters stabilized by various proteins and amino acids. Here, Mr. Sych demonstrates that the optimal conditions for synthesizing gold clusters are achieved with the same amount of gold atoms per stabilizing matrix, unlike silver clusters. The clusters exhibit a red emission maximum, with lifetimes in the microsecond range, and an additional maximum at around 410 nm. The clusters are formed under both alkaline and acidic conditions. Although potential candidates for stabilizing centers for gold clusters stabilized on protein matrices were not identified, the study provides a basis for further research in this field.

The fifth chapter is dedicated to the discussion of practical applications the aforementioned clusters, where Tomash shows that silver clusters stabilized with HSA and PGL matrices can be used to determine the concentrations of albumin and immunoglobulins in protein mixtures similar to blood serum. Gold clusters stabilized with HSA and PGL matrices can also be used for this purpose, exhibiting colorimetric selectivity for immunoglobulins. This method offers high precision and is faster and more cost-effective than current clinical diagnostic methods, which shows the importance of further research and application of metal fluorescent clusters stabilized by protein matrices.

I thoroughly enjoyed reading Mr. Sych's dissertation as it was well-organized, well-written, and demonstrated high-quality research that will undoubtedly contribute to the field of Condensed Matter Physics for the design and use of such clusters. Mr. Sych conducted a meticulous investigation of the subject matter, using carefully planned experiments and diverse analytical techniques to create, study, and characterize a novel system.

Based on the overall excellence of the thesis and the candidate's significant contribution to the field of Physics, I highly recommend accepting this Dissertation without mandatory corrections, as it meets all the criteria for a PhD thesis in terms of quality and quantity.

Диссертация Сыча Томаша Сергеевича на тему: «Люминесцентные кластеры благородных металлов, стабилизированные белковыми матрицами: фотофизические и структурные свойства, практические применения» соответствует основным требованиям, установленным Приказом от 19.11.2021 № 11181/1 «О порядке присуждения ученых степеней в Санкт-Петербургском государственном университете», соискатель Сыч Томаш Сергеевич заслуживает присуждения ученой степени кандидата физико-математических наук по специальности 1.3.8. Физика конденсированного

состояния. Нарушения пунктов 9 и 11 указанного Порядка в диссертации не обнаружены.

Член диссертационного совета

Ученая степень, ученое звание, должность, место работы:

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