R E P O R T

on dissertation work for obtaining the scientific degree "Doctor of Physical Sciences" in professional field 4.1 physical sciences (physics of atoms and molecules) in defense procedure at the Faculty of Physics (FzF) of Sofia University "St. Kliment Ohridski "(Sofia University)

The review was prepared by: Prof. Kiril Borisov Blagoev, in his capacity as a member of the scientific jury according to Order № .РД-38-15 / 15.03.2021 of the Rector of Sofia University.

Topic of the dissertation: "Energy Transport in Optically-Created Densely-populated Organic Triplet Ensembles"

Author of the dissertation: Assoc. Prof. Dr. Stanislav Balushev Balushev

I. General description of the submitted materials

1. Data on the submitted documents.

The candidate Stanislav Balushev Balushev presented a dissertation and an abstract, as well as the mandatory tables for the Faculty of Physics from the Regulations on the terms and conditions for acquiring scientific degrees and holding academic positions at Sofia University "St. Kliment Ohridski ". Two other documents were also presented - diplomas for completed higher education and for the scientific and educational degree "Doctor". The documents submitted for the defense by the candidate comply with the requirements of the Law on the Protection of Scientific and Technological Research, the Rules of Procedure and the Regulations on the Terms and Conditions for Acquisition of Scientific Degrees and Academic Positions at Sofia University "St. Kliment Ohridski" (PURPNSZADSU).

2. Professional and biographical data about the candidate.

Stanislav Balushev graduated in 1990 in the Faculty of Physics of Sofia University "Kl. Ohridski" in the field of laser physics. In 1998 defends a dissertation for the acquisition of the educational and scientific degree "Doctor" again in the field of quantum physics. He was

habilitated in the Faculty of Physics in 2009. Dr. St. Balushev was a part-time assistant at the Technical University 1991-1992, and during the period 1995 - 2003 is an assistant and chief assistant at the Technical University - Sofia. Since 2009 is an associate professor at the Faculty of Physics of Sofia University "Kl. Ohridski". Dr. St. Balushev was a guest researcher in a number of leading laboratories in the field of atomic physics - the Technical University - Graz; University of Hanover; University of Karlsruhe; Weizmann Institute; University of Braunschweik. He is the leader of a group at the Max Planck Institute for Polymer Research in Mainz. Marie Curie Fellow at the Advance Study Institute in Freiburg. Assoc. Prof. Dr. St. Balushev is a participant and principal investigator in 7 international projects; 2 projects under 7 FP and Horizon 2020, as well as 3 projects with NSF. Assoc. Prof. Balushev has lectured at the University of Freiburg; University of Mainz, Chalmers Soft Matter Grad School 2013, Rönnäng, Sweden.

3. General characteristics of the scientific achievements of the candidate.

Assoc. prof. Balushev works in the field of laser physics and technology and quantum optics. In recent years, his work has been in the field of sensitization luminescence of polyatomic molecules. The presented dissertation is also dedicated to this topic. The dissertation is written in English. It includes an introduction set out on 3 pages in which the problem is set and the main part of the dissertation, set out on 332 pages, including 303 figures and 12 tables. The material is divided into 12 chapters. The contributions are presented on 4 pages. The dissertation includes lists of the author's publications, on which the dissertation is created and a list of cited literature, including 336 titles. The abstract is written in Bulgarian and is set out in sufficient details on 141 pages. An insignificant number of technical errors can be noticed in the abstract. The dissertation is based on 33 articles and 12 patents and has been tested with reports at 14 international conferences. The materials are published by Assoc. Prof. St. Balushev co-authored with one or more co-authors.

Information about the author's contributions to publications with more authors is presented. Scientific publications have been published in high-ranking journals: The J. of Chem. Letters; ChemPhysChem; J. Org. Chem .; J. Am. Chem. Soc.; Advanced Materials; Appl. Phys. Letters; Nano Letters; Phys. Rev. Letter .; J. Appl. Phys. The list of publications also include 2 chapters from books; 1 review paper and 2 papers published in SPIE proceedings. The total number of citations of the works of Assoc. Prof. St. Balushev is 2463; the h-factor is 25. These data show the scientific and scientific-applied value of the publications of assoc. prof. St. Balushev. The scientific publications included in the dissertation meet the minimum national requirements (under Art. 2b, para. 2 and 3 of ZRASRB) and respectively the additional requirements of Sofia University "St. Kliment Ohridski "for obtaining the scientific degree" Doctor of Physical Sciences "in the scientific field of physics, professional field 4.1 physical sciences. The scientific publications included in the dissertation do not repeat those from previous procedures. I have not found legally proven plagiarism in the presented dissertation and abstract.

4. Analysis of the scientific and scientific-applied achievements of the candidate contained in the presentations of Assoc. Prof. Dr. St. Balushev dissertation work. The dissertation investigates the phenomenon of sensitization luminescence of complex molecules. During the excitation of triplet states and subsequent interaction of the excited triplet states, a transition to a high-lying radiating state takes place. During the radiative transition to the ground state, the sensitization fluorescence is observed, and the registered band has a higher frequency than the excitation light. The extra energy comes from the energy of the excited triplet ensembles. The phenomenon is observed in both monotypic and different types of molecules. This phenomenon is analogous to a process in atoms, but here the excitation is done with light, and the resulting radiation is also in the visible, near ultraviolet and IR region of the spectrum, but shifted to the

shortwave part of the spectrum relative to the excitation. Molecules of the porphyrin type doped with a metal atom - Pd, Pt, Zn, Cu - were studied. Clearly defined tasks, approaches to solving them and application of results should be noted. Depending on the set problems, the conditions that the molecules must meet are displayed - the mutual arrangement of their levels. The experiments record the absorption and emission spectra, their temporal evolution, their spatial distribution after irradiation with coherent light or continuum, for example sunlight. The conducted various experiments are at a high technological level and show the high experimental culture of the author. From a hardware point of view, no compromises are made both in the means of excitation and in the registration of the signals. Using the temperature dependence of the sensitization fluorescence, a temperature meter with significant spatial resolution was realized. By selecting suitable molecules as sensitizer, one or more in order to cover a wide spectral range of absorption and emitters for energy transfer in the shortwave part of the spectrum, it is possible to increase the efficiency of sunlight transducers. The use of 3 types of emitting molecules with energetically shifted radiation bands and one sensitizer molecule allows the realization of an optical reminder display. A laboratory model of the display has been implemented. The shift of the spectrum of sunlight to the shortwave part of the spectrum by a suitably selected sensitizer and emitter has been applied to increase the efficiency of photovoltaic devices. And here a laboratory model is realized. Triplet-triplet interaction and light conversion is used to increase the efficiency of photosynthesis, as infrared light is shifted to the green region, where bacterial photosynthesis is effectively realized. The role of the rotational diffusion of molecules in the triplet states is hypothesized, which explains the experimental fact of increased quantum yield and sensitivity to temperature changes. A strong temperature dependence of the fluorescence signal of sensitizer / emitter molecules dissolved in water has been shown, which are also more stable than those

dissolved in organic solvents. The presence of oxygen leads to the degradation of the processes discussed in the dissertation. Two methods have been proposed and implemented to eliminate this influence - encapsulation in nanoparticles and nanotubes or application of molecules sensitive to the singlet state of the oxygen molecule, which allows to create an oxygen sensor. The synthesis of suitable sensitizer / emitter molecules from biocompatible materials makes it possible to propose an intracellular Nano sensor of pathogenic cells for temperature and oxygen. In general, the work has the following sequence - registration of new phenomena; hypothesis about the nature of the registered spectra; synthesis of the necessary sensitizer / emitter molecules on the basis of the requirements for the necessary energy diagrams derived by the author; offering opportunities and implementation of a laboratory model.

5. The results obtained in the dissertation work have the character of observation of new phenomena, statement of new hypotheses, realization of new methods and creation of laboratory devices and sensors. Most of the results are protected by patents.

6. In the documents the applicant submitted 106 citations from other authors and "more than 400" was written. According to the SCOPUS database, the works from the dissertation have been cited 1745 times by other authors. In the documents, the author has described his specific contribution to the work with more authors.

7. In the dissertation I have noticed several technical errors: there is an error in the indication in fig. 2.2; in my submitted copy of the dissertation figures 8.13a and 8.14a, b are missing, which is a technical error, as these figures are available in the abstract; on page 62 of the abstract (or 172 pages of the dissertation) in the text is given a current density of 1.2 mA / cm^2, and on fig. 6.3a is given a current density of 2.2 mA / cm^2, which according to the author is the

correct value. These errors are technical in nature and do not affect the scientific and scientific - applied contributions of the dissertation. The abstract reflects the content of the dissertation.

8. Personal impressions of the candidate I know Assoc. Prof. St. Blushev since. I had the opportunity to discuss with assoc. prof. Blushev some of the problems presented in the dissertation.

9. Conclusion

After getting acquainted with the presented dissertation, abstract and other materials and based on the analysis of their significance and contained in them scientific and scientific-applied contributions, I confirm that the scientific achievements meet the requirements of ZRASRB and the Regulations for its application and the respective Regulations of Sofia University "St. Kliment Ohridski" for obtaining the scientific degree "Doctor of Physical Sciences". In particular, the candidate satisfies and significantly exceeds the minimum national requirements in the professional field and no plagiarism has been established in the dissertation, abstract and scientific papers submitted at the competition.

II. OVERALL CONCLUSION

Based on the mentioned above, the science metric data of the author, the high scientific and scientific-applied level of the results, as well as their practical application I fully suggest to the scientific jury to award the scientific degree "Doctor of Physical Sciences" in professional field 4.1 Physical Sciences (Physics of Atoms and Molecules) to Associate Professor Dr. Stanislav Balushev.

19 May 2021

Prepared by the review:

Prof. DSc Kiril Blagoev