REVIEW

of a dissertation paper

for acquiring the scientific degree of *Doctor of Physical Sciences*

in the professional field of Physical Sciences (Physics of Atoms and Molecules),

by a defense procedure at the Faculty of Physics

of *St. Kliment Ohridski* Sofia University (SU)

The review was prepared by Prof. Georgi Lalev Dyankov, PhD, Institute of Optical Materials and Technologies - BAS, in his capacity of a member of the scientific jury, according to Order № RD-38-148 of 15 March, 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: **Stanislav Balushev Balushev**

I. General description of the submitted materials

1. Information about the submitted documents

The candidate Stanislav Balushev has presented a Dissertation and a Synopsis, as well as the tables obligatory for the Faculty of Physics, taken from the Regulations on the Conditions and Order for Acquiring Scientific Degrees and Occupying Academic Positions at *St. Kliment Ohridski* Sofia University. A curriculum vitae and diplomas of completed higher education and the educational and scientific degree of Doctor of Philosophy have also been presented.

The documents submitted for the defense by the applicant comply with the requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria and the Regulations for its application, as well as the Regulations on the Conditions and Order for Acquiring Scientific Degrees and Occupying Academic Positions at Sofia University (RCOASDOASU).

2. Details of the applicant

The professional biography of the candidate is impressive. He graduated from the Faculty of Physics at Sofia University in 1990 with honors. He acquired his PhD degree in 1998

and attained his academic rank of Associate Professor in 2009. As a student he specialized in the research department of Lambda Physics in Germany. As a PhD student he specialized for about a year at the Institute of Quantum Optics in Hannover and the Institute of Experimental Physics in Graz. His PhD thesis is in the field of nonlinear optics. All publications related to the PhD thesis are in journals of the First Group (according to the additional requirements of the Faculty of Physics). In the years before attaining the academic rank of Associate Professor the candidate participated in projects as a visiting scientist - in the field of Bose-Einstein condensate (one year in Israel) and in the field of "cooled atoms" (one year in Germany). From 2001 to 2009 he held the prestigious position of a group leader at the Max-Planck Institute for Polymer Research.

The applicant attained the academic rank of Associate Professor on the basis of 16 articles published in prestigious journals, such as *Appl. Phys, Phys. Rev. A, Applied Physics Letters, Advanced Materials*, etc., all in Group One (according to the additional requirements of Faculty of Physics).

The present DSc dissertation includes papers that were published in the period 2011-2018, as well as patents that were registered in the period 2009-2015. Some of the papers were published when the applicant worked at the Freiburg Institute for Advanced Studies as a Senior Fellow (2014-2015).

In the period 2003-2021 the applicant participated in 9 projects with international and 3 with national funding.

All this shows the dynamic professional growth of the candidate, which has been acknowledged by prominent research centers in Europe and as a result of which he has held prestigious positions. Participation in projects funded by the Max Planck Society, SONY, the Marie Curie Program, the Seventh Framework Program, show the high scientific authority the applicant possesses.

3. General characteristics of the candidate's scientific achievements

The candidate's scientific achievements are in the field of physics of atoms and molecules; in particular, energy transport in densely populated organic triplet ensembles and especially the process of non-coherent annihilation up-conversion.

The scientific publications included in the DSc dissertation are 21 publications and 9 patents. Four publications are from group III, two publications are book chapters, and all other publications belong to group I, category Q1. In 17 of the publications the applicant has a significant contribution.

All patents are global, active, and in 7 of them the applicant has a significant contribution.

In Table 6 the applicant has listed his activities in publications and patents, in which he has not made a major contribution.

The number of points required by index D is exceeded almost 7 times.

The number of citations of the publications included in his DSc dissertation is more than 400, surpassing four times the requirements. The h-factor exceeds 6 times the required minimum.

The DSc dissertation includes 13 conference papers, 5 of which are invited.

Thus, the candidate repeatedly covers both the minimum national requirements and the additional requirements for acquiring scientific degrees at the Faculty of Physics of Sofia University.

In Table 3, the applicant presents information on the publications used in acquiring his PhD degree, the position of Senior Assistant Professor and the academic rank of Associate Professor. Articles published before 2009 are used for the Assoc. Prof. procedure, while publications after 2011 are used for the DSc degree procedure. Although formal, this criterion clearly shows that there can be no repetition of previously used results, as the publications included in the DSc dissertation are after 2011. The analysis of the content of the presented publications, their being published in prestigious journals and cited unequivocally show that these are new and original scientific results. The conclusion about absence of plagiarism in the presented dissertation and synopsis is categorical.

4. Characteristics and assessment of the teaching activity of the candidate (if there is a requirement in RCOASDOASU for this)

There are no requirements for educational and pedagogical activities of the candidate.

5. Content analysis of the scientific and the scientific and applied achievements of the candidate contained in the materials for participation in the competition

The scientific achievements in the dissertation consist in the formulation and experimental proof of several hypotheses:

1. The hypothesis that the dynamic characteristics of the TTA-UC process in a soft matter matrix differ drastically from the classical descriptions.

The correctness of this hypothesis allows:

- to reduce the intensity of the excitation light more than 6 orders of magnitude;

- to use low spectral power density of incoherent light (solar radiation).

2. The hypothesis that increasing the temperature of the optically inactive or optically active matrix of soft matter leads to a decrease in viscosity, which in turn leads to a temperature-dependent increase in the local mobility of the dispersed molecules and faster finding the optimal steric arrangement and ultimately to a significant temperature-dependent increase in the intensity of delayed fluorescence, i.e. to a more effective TTA.

The testing of this hypothesis gave rise to the idea

- of all-optical temperature sensing in thin layers;
- of two-dimensional temperature measurement of two-dimensional objects based on the technique of confocal microscopy (patented).

3. Formulation of the hypothesis of selecting the rules for TTA-UC. Empirically, rules have been formulated for the selection of the parameters of the singlet and triplet energy states of the optically active dyes, which guarantee high quantum yield in a soft matter.

The reliability of the hypothesis is proved by:

- Experimental demonstration of incoherent sunlight TTA-UC excitation for the first time in the world (patented).
- Experimentally proving the statement that combining different sensitizers, each of which efficiently working with the same specific emitter, indeed can work in ensemble with the efficiency at least equal to the single one.
- The synthesis of a series of porphyrins which allows adjustment of the TTA-UC spectrum; this in turn allowed the creation of the world's first all-organic, transparent, flexible, versatile color display based on TTA-UC; this also allows the displacement of IR limit of oxygenic photosynthesis.
- A very high quantum yield of 0.11 was obtained on TTA-UC.

4. Formulation of the hypothesis that molecular rotational diffusion is the origin of the huge distances of triplet energy diffusion. It has been experimentally proven by quantum yield and temperature sensitivity of TTA-UC in a soft matter matrix.

5. Formulation of the hypothesis that the efficiency of the TTA process in a soft matter matrix also depends on the local mobility of the participating dye molecules.

The reliability of the hypothesis was proved by measuring the local temperature, which is commented above.

The experimental proof of the hypotheses formulated in the dissertation is a significant contribution to the field of research. New regularities have been discovered, new knowledge

has been formulated, which has allowed the experimental realization of the unique non-coherent up-conversion.

The experimental realization of the proven hypotheses demonstrates an extremely high experimental competence in a complex interdisciplinary field, in which the applicant is a leading scientist.

The scientific and applied achievements included in the dissertation, excluding the already mentioned patented contributions, are as follows:

1. Implementation of TTA-UC in nano-confinement – micelles, which leads to sustainable monitoring of up-conversion in water environment. The sensory properties of the micelles have been demonstrated, as they have been used for temperature sensing allowing exceptional temperature sensitivity. The various core-shell polymer nanocapsules synthesized, performing efficient TTA-UC, allow for bio-imaging with deep-red light penetrating the tissues, which is also a unique experimental achievement (patented).
2. A series of substances have been synthesized, allowing the protection of triplet states from photooxidation. Protection has been achieved by temperature-controlled addition of singlet oxygen to a specially synthesized "tail" of the solvent. Thus, for the first time, TTA-UC has been performed for an extremely long-term period in oxygen-saturated environment. The achievement has been patented. A quasi-solid matrix based on cellulose nanofibers has been synthesized in which incoherent TTA-UC has been performed. The achievement has been patented.
3. Nanosensors based on TTA-UC have been created, through which simultaneous and independent measurement of temperature and oxygen content applicable in cells has been performed. Minimally invasive, all-optical sensing of oxygen concentrations ranging from normoxia to severe hypoxia has been achieved, which is a significant technological achievement. High sensitivity measurement of local temperature has also been achieved.

The scientific achievements presented in the dissertation are a combination of fundamental research and practical implementation. A complete consistency in research in an interdisciplinary field has been achieved, which requires deep knowledge and extensive experimental experience from the applicant.

The dissertation is written in a fascinating way, revealing the logic of the development of scientific ideas and the sequence of research. Methodologically, the material is well-formed:

the introductory and concluding notes to the chapters / paragraphs of the dissertation facilitate the reader and provide additional information with methodological focus.

6. Critical remarks and recommendations

I have no critical remarks on the Dissertation and the Synopsis.

7. Personal impressions of the applicant

I have mediated impressions of the applicant through colleagues and common acquaintances for the last 15 years. Feedback and comments have always been positive, both in terms of scientific activity and achievements, and as personal qualities.

I have been following the candidate's publications for years and I highly appreciate his scientific activity, aimed at solving significant fundamental problems and striving for practical realizations, solving technological challenges.

8. Conclusion

After getting acquainted with the submitted Dissertation, Synopsis and other materials, and based on the analysis of their significance and the scientific and scientific and applied contributions contained in them, **I confirm** that the scientific achievements meet the requirements of the Law on the Development of the Academic Staff in the Republic of Bulgaria and the Regulations for its application and the relevant Regulations of Sofia University "St. Kliment Ohridski" for acquiring **the scientific degree of Doctor of Physical Sciences**. In particular, the candidate satisfies the minimum national requirements in the professional field and no plagiarism has been established in the dissertation, synopsis and scientific papers submitted at the competition.

I give my positive assessment of the dissertation.

II. OVERALL CONCLUSION

Based on the above, I **recommend** the scientific jury to award the **degree of Doctor of Physical Sciences** in the professional field of **Physical Sciences (Physics of Atoms and Molecules)** to Stanislav Balushev Balushev.

30 May, 2021 Review prepared by: ..... .

Prof. Georgi Lalev Dyankov, PhD