

## Review

**Subject:** competition for associate professor in the scientific specialty "Organic Chemistry", a professional field for the needs of the Department of "Organic Chemistry and Pharmacognosy" at the Faculty of Chemistry and Pharmacy of Sofia University "St. Kliment Ohridski"-Sofia.

**Candidate:** chief Assistant Professor Dr. Stanislav Stefanov Stanimirov "Department of Organic Chemistry and Pharmacognosy" at the Faculty of Chemistry and Pharmacy, Sofia University "St. Kliment Ohridski "- Sofia.

**Reviewer:** Professor Tsonko Mitev Kolev, Institute of Molecular Biology - BAS

### I. General description of the submitted materials

In the competition for associate professor in the scientific specialty "Organic Chemistry", at the Department of Organa Chemistry and Pharmacognosy at the Faculty of Chemistry and Pharmacy of Sofia University - "St. Kliment Ohridski "Sofia, only one candidate participates - Dr. Stanislav Stefanov Stanimirov. For participation in the competition the candidate has submitted a complete set of documents in accordance with the requirements of the Regulations on the terms and conditions for obtaining scientific degrees and holding academic positions at the Faculty of Chemistry and Pharmacy, Sofia University. Kliment Ohridski "- Sofia. The materials are carefully prepared and very well systematized.

- European CV format;
- Copy of the diploma for the educational and scientific degree "Doctor";
- Medical certificate;
- Certificate of criminal record;
- Certificate of internship in the specialty (copy)
- Certificate from the last place of work for teaching activity and workload,
- List and copies of publications in specialized scientific journals (articles, monographs, teaching aids);
- Published study materials - textbooks, collections, manuals, etc., developed by the candidate,
- Evidence of participation in research projects (official notes, contracts for participation in research teams, etc.);
- Official note for work on a curriculum or a course of teaching in a higher school;
- List of participations in scientific forums (congresses, conferences, symposia), accompanied by a copy of the title page and the summary of the booklet with the summaries of the forum;
- List of citations (only publications in specialized scientific journals are considered) and abstracts of papers after defense of the doctoral dissertation (on paper and electronic media);
- Information on participation in editorial boards, membership in an authoritative creative and / or professional organization in the respective scientific field, reviews,

publications of public importance, etc. achievements with the signature of the candidate;

- Author's reference of the scientific contributions of the works;
- Habilitation work;
- Others.

1. PERSONAL INFORMATION Name: Stanislav Stefanov Stanimirov. Date of birth: 20/09/1979 Nationality: Bulgarian. Business address: J. Boucher "1, Faculty of Chemistry and Pharmacy, Sofia University" "St. Kliment Ohridski", 1164 Sofia. Phone: (+ 359-2) 81-61-451 E-mail: sstanimirov@chem.uni-sofia.bg

2. EDUCATION 1998-2002 Bachelor, Sofia University, Faculty of Chemistry, Sofia

3. from 2003 to 2007 he is a doctoral student. Acquired ONS Doctor, in 2007. Scientific specialty: Organic Chemistry, code 01.05.03 Sofia University, Faculty of Chemistry, Sofia Topic: "Synthesis and photophysical properties of ternary  $\beta$ -dicarbonyl europium complexes with nitrogen-containing or poly (oxyethylene phosphate)" supervisor: Prof. Ivan Kolev Petkov

4. WORK EXPERIENCE 2009 - so far Sofia University "St. Kliment Ohridski", chief assistant. 2008 - 2009 Sofia University "St. Kliment Ohridski", assistant.

5. 2007 - 2008 Sofia University "St. Kliment Ohridski", chemist.

6. RESEARCH ACTIVITY Total number of publications - 19 Publications in journals with impact factor (IF) - 19; total IF = 33.268; publications in Q1 - 6; publications in Q2 - 5; publications in Q3 - 6; publications in Q4 - 1; without quartiles - 1.

7. Total number of citations - 125 - Author ID, (SCOPUS): 6504206907 - ORCID ID: 0000-0001-7891-832X - Google Science URL: Stanislav Stanimirov

8. LEARNING ACTIVITY: Lecture courses in Organic Chemistry - specialty Agrobiotechnology (BF), full-time education, Compulsory. Organic photochemistry - specialty Chemistry (FHF), part-time study, Compulsory.

9. Practical classes: Seminars and exercises in Organic Chemistry I and II - all specialties of FHF and BF, full-time and part-time training. Seminars and exercises in Organic Photochemistry - all chemical specialties of FHF, full-time and part-time education.

10. SHORT-TERM SPECIALIZATIONS 2018 -2019 Swansea University, Swansea, UK Six months research assistant in the group of Dr Matthew Davies and Professor James Durrant.

11. 2015 MPIPF Mainz, Germany One month specialization in the group of prof. H. -J. Butt on the project "Beyond EVEREST".

12. 2014 MPIPF Mainz, Germany One month specialization in the group of prof. H. -J. Butt on the project "Beyond EVEREST".

13. 2013 MPIPF Mainz, Germany One month specialization in the group of prof. H. -J. Butt on the project "Beyond EVEREST".

14. 31.05 - 04.06.2010 Principles of fluorescent techniques - Madrid Spain Summer school under the guidance of prof. Enrico Gratton and prof. Dave M. Jameson.
15. Specialization 2009 Boston College, Boston USA, One month
16. specialization in the group of prof. Torsten Fiebig. 2008 MPIP Mainz, Germany
17. One month specialization in the group of prof. H. -J. Butt on the DAAD program. 2007 MPIP Mainz, Germany
18. Two months of specialization in the group of prof. H. -J. Butt by DAAD program Organic Photochemistry - specialty Chemistry (FHF), full-time education.

As can be seen from the attached list, the candidate has significant experience in institutes and universities in the UK, USA and Germany, which led to his growth as a specialist in electron spectroscopy: UV-vis and Fluorescence spectroscopy.

**PARTICIPATION IN THE CONFERENCE (sample).** Workshop "Synthesis and Characterization of Nano-materials" 03 - 06 April, 2014 Festa Chamkoria Hotel, Borovets, Bulgaria Stanislav Stanimirov Emptying the  $\beta$ -cyclodextrin cavity by light. Photochemical Removal of the trans-chalcone of 4', 7-dihydroxyflavylium." Second International Conference "Advanced Functional Materials" 3 - 6 September 2014, Sol Nessebar Resort, Bulgaria Stoyanka Slavcheva, Stanislav Stanimirov, Veselin Petrov, "Influence of  $\beta$  cyclodextrin complexation over multi equilibria of 2- (4-hydroxyphenyl) chromenylium cation". III Scientific Conference of the Faculty of Chemistry at Sofia University "St. Kl. Ohridski" November 21, 2011 St. Stanimirov, "Femtosecond laser spectroscopy - a tool for studying ultrafast molecular processes." Principles of Fluorescence Techniques 2010 Madrid, Spain S. Stanimirov, A. Trifonov, "The excited states lifetimes, efficiency of energy transfer and quantum yields of the ternary Eu (III) complexes". 2nd International Symposium on Organic Chemistry, December 2008, Sofia, Bulgaria S. Stoyanov, S. Stanimirov, I. Petkov, S. Saltiel, Y. Sheng, K. Koynov (Bulgaria, Germany) "Second and third harmonic generation with styryl pyridines containing thin polymer film

It should be noted that - Dr. Stanislav Stefanov Stanimirov has participated in the above scientific activities and has reported on the possibilities of femtosecond laser spectroscopy - a tool for studying ultra-fast molecular processes ", which shows that the topics he developed are relevant and his achievements are significant. This makes him a serious candidate for the academic position of "Associate Professor".

**PARTICIPATION IN PROJECTS :** Participation in over 15 research projects funded by the Research Fund - MES, and various national and European Operational Programs. Head of the partner organization of a project to the operational program "Innovation and Competitiveness".

His participation in these research projects, funded by the Research Fund - MES, and various national and European Operational Programs makes Ch. Dr. Stanislav Stefanov Stanimirov led to his growth as a specialist in electron and special fluorescence spectroscopy and this modern method is a tool for studying ultra-fast molecular processes, which are the basis of modern physical organic chemistry. The applicant meets the minimum national requirements under Art. 2b of ZRASRB for scientific field 4. for holding the academic position "Associate

Professor" Natural Sciences, Mathematics and Informatics, professional field 4.2. Chemical Sciences (Organic Photochemistry), With a minimum national required of 200 points and required by the faculty of 220, it has 246 points.

The candidate's habilitation thesis entitled: INVESTIGATION OF THE INFLUENCE OF LEWIS LIGAND ON QUANTUM YIELD OF TERNARIAN  $\beta$ -DICARBONYL EUROPEAN COMPLEXES WITH THE HELP OF EXTREMELY FAST TRANSIENT ABSORPTION.

His habilitation thesis was developed on the basis of his latest article, included in the competition for associate professor. This study shows the direction of development of the research interests of the candidate in the years after the defense of his doctoral dissertation. On the one hand, it includes a study of the properties of photo and electroluminescent complexes of Eu (III) with  $\beta$ -dicarbonyl organic ligands, a topic he has been developing since his doctoral studies, and on the other hand it is a demonstration of the capabilities of ultrafast femtosecond transient absorption spectroscopy. tool for studying the dynamics of relaxation of the photoexcited state of molecules. The construction of the Laboratory of Molecular Dynamics and Transient Absorption at Sofia University began after 2009. Since then, the development of this unique laboratory in Bulgaria and the mastery of the theory related to the analysis of complex spectroscopic data, he accepted as a personal vocation. I definitely think that this article is valuable and the construction of the habilitation work on it is largely justified. The habilitation work is structured in the classical way, which includes: Preface, Introduction, Results and discussion, Structure of complexes, Transient absorption spectra and dynamics of relaxation of the excited state of DBM (dibenzoylmethane) complexes, Conclusion, Experimental data, References. The study of the structure of the complexes with the help of IR spectroscopy is logical as it can be performed in the solid state. The data from these spectra are shown in Figure 1 on page 11 in the habilitation work. These data were compared with those of Pinchas, Silver, and Lulith [34] S. Pinchas, B.L. Silver, I. Laulicht, Infrared Absorption Spectra of the  $^{18}\text{O}$  - Labeled Acetylacetonates of Cr(III) and Mn(III), The Journal of Chemical Physics, 46 (1967) 1506-1510. The use of  $^{18}\text{O}$ -labeled compounds is unambiguous in the reference to valence and strain oscillations involving a carbonyl group. Unfortunately, this publication is quite old, but there are no newer works in the literature. I recommend to Ch. Assistant Professor Dr. Stanislav Stanimirov in future research on DBM complexes to use modern IR absorption spectra. In the analysis of the dynamics and relaxation of the excited state of DBM (dibenzoylmethane) complexes, the candidate skillfully interprets the data from the electronic spectra and critically treats some data. Scheme 1 on page 16 and Scheme 2 on page 17 make a very good impression. The latter scheme shows the transient absorption of DBM in ethanol at 23 ° C excited with 350 nm. a) are the representative spectra of the compartments (SAS) and b) - the fit of the kinetic curves at selected wavelengths obtained after the target analysis of the transient matrix -c). The deleted part around 350 nm contains optical artifacts from the excitation. I pay attention to this part of the study because in the photophysical studies of my group on styrene dyes with extended  $\pi$ -electron system we observed similar phenomena. Despite serious research in solutions, Dr. Stanimirov and co-authors seek explanations for the observed photophysical phenomena using spectra of polymer films doped with the studied compounds and deposited on quartz glasses. Fortunately, samples containing DBM and  $\text{Al}(\text{DBM})_3$  complex, show phosphorescence at room temperature. The fluorescence and phosphorescence spectra of excitation and emission of  $\text{Al}(\text{DBM})_3$  complex in the polymethyl methacrylate (PMMA)

matrix are presented in Figure 6 and Figure 7, respectively. The authors show that the quantum yield of phosphorescence is higher at 260 nm excitation and even in the polymer matrix the test connection of the first singlet state (accessible by excitation with 350 nm) with the triplet state is weak. However, the excitation spectrum of the phosphorescence clearly shows a visible phosphorescent signal upon excitation at 340 nm, which proves the existence of the triplet state. The study of the TA dynamics of complexes with nitrogen-containing ligands shows a clear relationship between the efficiency of energy transfer and the settlement of the triplet state. The replacement of the water molecule by the  $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$  complex with a nitrogen-containing ligand acts as a 'switch', including the ICC as an efficient channel for energy transfer to the  $\text{Eu}(\text{III})$  ion. In addition, after analyzing the TA data, we conclude that ligand replacement not only "includes" the ICC, but also changes the relative efficiency of transitions and population proportionality constants between singlet excited states. Stanimirov and co-authors found that the effective settlement of the third compartment of the singlet state is essential for the settlement of the triplet level. In the case of the  $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$  complex, 85% of all excitations are lost in the first two compartments. Although there is some population in the third singlet compartment of this compound, by analyzing its TA spectrum we found no evidence of a triplet excitation population. In addition to the spectral contributions, habilitation work also has purely synthetic contributions, such as the synthesis of  $\text{Eu}(\text{DBM})_3 \cdot (\text{H}_2\text{O})$  and the replacement of water molecules from the  $\text{Eu}(\text{DBM})_3 \cdot \text{H}_2\text{O}$  complex with nitrogen-containing molecules. It is noteworthy that the candidate and co-authors have worked with modern equipment as NMR spectra were measured on a Bruker Avance III 500 NMR spectrometer in solutions of chloroform and acetonitrile. The FTIR spectra of the complexes were measured on a Shimadzu 8400S FTIR spectrometer in a KBr pellet. Absorption spectra were recorded on an Agilent Cary 5000 UVVIS-NIR spectrophotometer. Emission spectra and fluorescence lifetimes were measured on an Agilent Cary Eclipse fluorescence spectrophotometer. The luminescent quantum yields were determined with a TCSPC spectrophotometer from the Horiba Fluorolog 3 series, equipped with an integration sphere for measuring quantum yield and CIE, Quanta-phi. The polymer films were applied to a glass substrate using a WS-400B-6NPP Spin Coater. The transient absorption spectra were captured with a unique "Pump-sample" installation working with white light, practically identical to the one with which the authors worked earlier. The excitation wavelength is 350 nm for all samples. Changes in optical density were examined from a femtosecond white light continuum (WLC) generated by focusing a small fraction of the output (790 nm) of commercial Ti: sapphire based laser (Integra-C, Quantronix) in a 3-mm rotating calcium fluoride disk. WLC is a usable source for spectral studies in the range between 320 and 750 nm. WLC was divided into two beams (sample and reference) and focused on the sample using reflective optics. After passing through the sample, both beams are focused on a CCD sensor. The pulse (1 kHz, 300 nJ) is generated by doubling the frequency of the compressed output of a non-commercially constructed non-collinear optical parametric amplification system (700 nm, 9  $\mu\text{J}$ , 40 fs). An additional prism compressor was used to compensate for the dispersion of the group velocity in the UV pulse. The total resolution during the system is determined by the cross-correlation function between the excitation and measurement pulses, which is between 110 and 130 fs (fwhm, assuming the pulse has a Gaussian shape). Spectral resolutions of about 5 nm were obtained for the entire spectral range. All measurements were made at a magic angle of (54.7 °) between the polarizations of the pump and the test pulse. I pay attention to these experimental details because they determine the quality of the experiment. My conclusion about the habilitation work is positive and it shows the growth and formation of Dr. Stanislav Stanimirov as a

specialist in the field of fluorescence and phosphorescence spectroscopy as well as femtosecond laser spectroscopy for the study of ultrafast molecular processes.

## **II. Critical remarks and recommendations**

When reviewing the current habilitation thesis and other documents, I found no significant errors in terms of: staging; analyzes and generalizations; methodological level; accuracy and completeness of the results; literary awareness. I found only inaccuracies in the spelling of some words such as transient spectroscopy. It is right for our physicists to introduce an appropriate Bulgarian word, unfortunately such a translation is missing and we are forced to use such words. I noticed typographical errors and stylistic errors. All noticed mistakes are irrelevant and do not change my high opinion about the qualities of the habilitation work. And the other materials submitted for the competition.

## **Conclusion**

After getting acquainted with the presented documents, habilitation work, 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 implementation and the relevant Regulations of Sofia University "St. Kliment Ohridski "for acquiring the academic position of Associate Professor". In particular, the candidate satisfies the minimum national requirements in the professional field and no plagiarism has been established in the habitation work and scientific works submitted at the competition.

I give my positive assessment of the habilitation work.

## **III. OVERALL CONCLUSION**

Based on the above, I strongly recommend to the scientific jury to award the academic position of "Associate Professor" in the professional field 4.2 Chemical Sciences. (Organic Photochemistry). Dr. Stanislav Stefanov Stanimirov from the Department of Organic Chemistry and Pharmacognosy at the Faculty of Chemistry and Pharmacy at Sofia University "St. Kliment Ohridski ”.

November 2, 2021

Prepared the review.....  
(Prof. Tsonko Kolev)