Skoltech
Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Julia Bondareva

PhD Program: Materials Science and Engineering

Title of Thesis: Sulfonimide-based dendrimers: synthesis and application for surface functionalization

Supervisor: Associate Professor Igor Shishkovsky

Name of the Reviewer: Prof. Alexei Buchachenko

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Signature:**  **Date: 05-09-2020**

The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense

The Thesis submitted by Julia Bondareva to fulfill the requirements of the Skoltech PhD degree in Materials Science and Engineering is devoted to the synthesis of the sulfonimide-based dendrimers in solution and formation of their films. The results can be attested as quite an achievement, as it turned to be possible, by brilliant combination of synthetic strategies, to go up to 5^{th} dendrimer generation. Careful optimization of the synthetic routes and conditions makes it possible to produce desirable substances in an amount enough to form good quality films by Langmuir-Blodgett method and transfer them to solid substrate for further investigation. UV radiation was used to film modification converting non-bonding interactions to covalent bonds. Film morphology and properties, such as thickness, Young modulus, wettability, UV and optical response, were characterized. I dare to say that the Thesis documents the development of a new hydrophobic coating material with potentially well-controlled properties. Of course, it would be instructive to learn how the synthesis can be scaled, how the parameters of Langmuir-Blodgett approach can be adjusted to achieve better morphology, how the film properties change with the dose of UV radiations and many other aspects. However, one should realize that such a tuning of commercially interesting materials usually takes years of efforts for a few research groups, so certainly may not be accomplished within a single doctoral project.

The good level of the research is certified by the scientific publications. Three papers were published in well-known organic chemistry journals, while the fourth one appeared in high-impact *Applied Surface Science*, Q1 journal for coating materials, films, and physical chemistry of interfaces. It signifies an interest to new dendrimer films in the broad scientific community.

Evaluating the scientific merit of the Thesis quite high, I cannot do the same for the presentation. Unfortunately, the writing is generally vague, sometimes logically disconnected, sometimes repetitive, sometimes stylistically improper. Below I am summarizing the most evident issues that deserve to be addressed prior to the defense.

1. The Thesis does not set the overall goals of the work. Clear formulation of the goal normally sets the logic of the work and text and establishes its integrity by connecting different pieces in a coherent document. Otherwise, it is difficult to the reader (and reviewer) to apprehend the main targets to be achieved, main tasks to be solved, main messages to be taken. Moreover, the lack of goals undermines the value of the results and masks the novelty of conclusions of the work. *I strongly suggest to rewrite introductory Chapter 1 adding clearly formulated research goals of the PhD project.*

2. Introductory Chapter strongly overlaps with the literature review (Chapter 2). Misleading is the placement of the potential applications of the sulfonimide-based dendrimers on the front cartoon (Fig.1) prior to exposure of a general landscape and essential relation between the physico-chemical properties and the particular field of application. The properties of dendrimers under study and other dendrimer families are compared to some extent in Chapter 2. The niches suggested for a new family can thus be rationalized only afterwards. Patent analysis also comes too early. Moreover, it hints that the Thesis will address particular applications and reveal commercialization prospects. Nothing fits these expectations. It is not clear why the works considered in Section 1.2 are “related” – this can only be substantiated by clear formulation of

the goals. *I suggest to make introductory Chapter more concise setting the goals and explaining them by indicating what specific features are expected from the sulfonimide-based dendrimers. Further details, including patent analysis, are more appropriate in the Section 2.1.7 - Application of dendrimers.*

3. Section 3.1 does not look instructive. Undoubtedly, synthetic protocols described therein to a degree allowing for reproduction are extremely valuable. However, being disconnected from the graphical schemes in Chapter 4, they only break the text flow. *I suggest to present Section 3.1 as an Appendix and rearrange the rest and current Chapter 4 into two Chapters, one for essential synthetic information decorated with schemes, another for film preparation and characterization.*

4. *During the revision of the Thesis, I do recommend the author to keep in mind general goals and refer to them whenever appropriate.*

Let me repeat that these critical comments, no matter how tough they look, address the presentation aspects. The work done by Julia Bondareva certifies her as a qualified researcher with experience in both organic and surface chemistry, who mastered modern synthetic and characterization techniques. I think that the Thesis submitted can be brought to the defense after revision.

Provisional Recommendation

☐ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*

☒ *I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*

☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*