Review Report on PhD Thesis

Faculty: **Central European Institute of Technology**
Brno University of Technology in Brno

Academic year: **2024/2025**

Student: **Ing. Tomáš Krajňák**

Doctoral study program: **Advanced Materials and Nanosciences**

Supervisor: **prof. Ing. Jan Čechal, Ph.D.**

Reviewer: **Dr. Nataliya Tsud**

PhD thesis title: Structure of tricarboxylic acids on metal surfaces

Topicality of doctoral thesis:

This doctoral thesis focuses on the study of tricarboxylic acid layers on silver single crystals using state-of-the-art surface science techniques. This challenging research topic is primarily related to the development of advanced materials for novel components in organic electronics, sensors, and energy storage systems — fields that are constantly evolving in line with technological progress.

Meeting the goals set:

The original idea was to use tricarboxylic acid layers as charge-injection interfaces in homostructures or heterostructures formed on a metal electrode. To achieve this, it was necessary to properly characterise the molecular layer on the metal surface. This was successfully accomplished by applying a variety of microscopic and spectroscopic surface science techniques.

Problem solving and dissertation results:

The thesis begins with a brief introduction to the research topic, focusing on aspects of molecular self-assembly and non-covalent interactions, emphasising their importance in developing new approaches to component design for organic electronics. The aims and objectives of the work could be stated more clearly in this section. It would also be helpful to include figures showing the molecules here, rather than in the Results Chapter. The thesis then goes on to describe the experimental techniques and methods used. This section contains all the information necessary for analysing the results of the experiments. However, it does not provide details on synchrotron radiation XPS measurements. The results of the thesis are reported in two chapters. In the Chapter 4, the author presents an analysis of single-component molecular films on the silver surfaces. Chapter 5 is dedicated to the studying of the second molecular film on the well-defined BTB layer on Ag(111). Finally, the results are summarized, providing an overview of the studied systems emphasising the important finding of a charge injection layer in the form of annealed BTB molecular films on silver single crystals.

Importance for practice or development of the discipline:

The most significant achievement of this thesis is the demonstration that annealed BTB molecular films on silver single crystals, independent of their orientation, form robust, stable, electron-rich layers with the potential to be used as charge-injection layers. This finding has been published in a high-profile journal. Furthermore, the results obtained on the TMA/Ag system complement the existing published information on this topic. The study also sheds light on how molecular films form and remain stable under different conditions. Additionally, it has been demonstrated that molecules in the second layer on the metal surface can be successfully characterised using LEEM/LEED and STM techniques.

Formal adjustment of the thesis and language level:

The reported results have been published in one high-impact international journal, and another paper is currently being prepared for publication, with Tomáš Krajňák as the first author of both papers. He is also the co-author of three other publications. The thesis is written in good English, although some sections could benefit from more detailed elaboration. I would like to emphasise that the presented work reports a large amount of data acquired using LEEM/LEED and STM techniques. This demonstrates the high level of expertise acquired by the author in experimental work during his doctoral study.

Questions and comments:

The questions I have about the thesis content are listed below in order of importance.

More important:

1) How might electron excess in the δ-BTB layer affect the stability of molecules in the second layers under study? What types of interaction could there be between the two layers?
2) Could you draw a diagram showing the interface between the δ-BTB layer and the silver substrate, indicating the different types of bond?
3) How did you check the integrity of the evaporated molecules?
4) Page 58: It is written "there is no active contact with metal substrate". What do you mean by this phrase? What is the role of the substrate in the deprotonation of the δ-BTB layer?
5) What happens to the protons after thermally induced deprotonation in the BTB/Ag systems?
6) Do you analyse the N1s core level for the HAT-CN molecular films?
7) Page 40: It is written "After annealing at 235 °C, the added BTB deprotonate and incorporate into the first δ-BTB layer". Did you consider the desorption of the molecules during the annealing?

Less important notes and corrections:

1) The abbreviations used in the text are introduced multiple times, with no clear logic applied to their usage.
2) Page 4: Description of the thesis division into 5 sections does not correspond with the numbering in the Contents. Furthermore, there are two chapters present the results of the study, rather than the one stated in the Introduction.

3) Page 6: “The interaction strenghts between molecules are compared in Figure 2.1.” should be written as “The interaction types and their bond strength are compared in Figure 2.1.”
4) Page 8: Cation – π interaction is shown in Figure 2.2c, not 2.2b.
5) Page 12: “… low pre-vacuum pressure of approximately 10^{-7} mbar” should be written as “... high vacuum pressure of approximately 10^{-7} mbar”.
6) Page 32: Figure 4.6 has swapped parts (a) and (b).
7) Throughout the thesis, temperatures should be expressed in either Celsius or Kelvin.
8) Page 54: Text repetition.
9) Page 70: “The further annealing up to 220 °C” should be “The further annealing up to 235 °C”
10) The references stile is not unified.

Conclusion:

In my opinion, the reviewed thesis fulfill all requirements posed on theses aimed for obtaining PhD degree. This thesis is ready to be defended orally, in front of respective committee.

Thereby, I recommend **Tomáš Krajňák** to be awarded **the title PhD**.

In Trieste, date 15.07.2025

....

Dr. Nataliya Tsud