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Prof. Dr. Mirko Rokyta
Dean
Faculty of Mathematics and Physics
Charles University Prague

Prague, May 18 2022

Dear Profs. Rokyta and Kulich, der Colleagues,

Following your request from May 13th, I am pleased to provide my report on the PhD thesis of **Aurelio Gallardo** "*Theoretical study of charge states in molecular nanostructures on surfaces*".

Overall, the PhD thesis was very successful with Aurelio being coauthor of ten publications in excellent journals. Out of these, there are four papers where he is first or equivalent author. The paper on black phosphorous (Phys. Rev. Lett. 2022) appeared only during writing of the thesis and is not included in the manuscript. The paper on binding and scanning probe microscopy visualization of planar halogen-benzene molecules (J. Phys. Chem. 2018) is appended and only briefly described in chapter 4 of the thesis. After an introduction to scanning probe microscopy and to the theoretical methods used to describe the forces between tip and sample and the tunnel current, the thesis presents the theoretical methods used, and then it focuses on the other two first author papers, the first reporting on the imaging of the sigma hole with Kelvin probe force microscopy (Science 2021) and the second on the isomerization of metal-organic chains, driven by strain (Angew. Chem. Int. Ed. 2019).

The work testifies a breath of different theoretical methods that the candidate perfectly manages. Some of them are entirely new to the field of surface science. One example is the combination of quantum mechanical and molecular mechanics simulations that are used to address the reaction barriers and the conformation of the transition state in the strain-induced isomerization of metal-organic chains. But also, the simulation developed to quantitatively understand the experimental Kelvin probe force microscopy (KPFM) results reporting the direct imaging of the sigma hole in tetrakis(4-bromophenyl)methane (4BrPhM) on a Ag(111) surface. The presented simulations of KPFM are new, they gave rise to a new module of the probe particle model developed in the group. Moreover, the experimental observation of the sigma hole is a significant breakthrough that gets strongly supported by

the theoretical model. Some of the tests and of the tip functionalizations seem to be inspired by the calculations and make the paper stronger. The PhD thesis thereby clearly proofs that the candidate is able to perform very creative scientific work. In looking forward to the defense and the discussion with the candidate.

With best regards,