17 January 2022, Prague

To whom it may concern,

Please find my assessment of PhD thesis entitled "*Electronic, mechanical and transport properties of molecular junctions*" presented by Narendra Prabhakar Arasu from Faculty of Mathematics and Physics, Charles University, Prague, Czechia.

The PHD thesis deals with a systematical computational study of structure, electronic, mechanical and transport properties for molecular junctions, done in a close collaboration with experimentalist. Candidate studied molecular with different properties, including donor-acceptor, carbenes, aromatic and antiaromatic molecules. By using advanced quantum-based calculations, candidate not only help experimentalists to well explain the experimental results in molecular junctions, but also provided deeper understanding of molecular junction to enable rational design and improvement of their transport properties towards molecular electronics.

The thesis is very well written and has a logical structure providing enough computational details. All chapters suitably start with a brief introduction and the contributions to the chapter and contained a summary of the main conclusion. The major achievements of the PhD-thesis of the candidate are reported in six top publications, such as prestigious journal *Nat. Commun.* and *JACS*, demonstrating the scientific capabilities of the candidate. The major research achievements include:

1) The structural and electronic properties for donor-bridge-acceptor molecule, carbazol and phenalenon adsorbed on Pt(111) surface platinum substrate are systematicly studied. Their results suggest that the molecule maintains many donor-acceptor characteristics, facilitating the carrier separation in organic solar energy device.
2) The authors systematically studied carbene molecule adsorpted on Au surface. And they further found the tilted adsorption of the carbene molecule study attributed to the high electronegativity of the carbene core. The molecule showed stronger adsorption than any other carbene previously studied, opening an new way to investigate the carbene-based surface science.
3) Authors studied mechanical and electron transport properties biphenylene-based bipodal molecular junction with respect to different linker groups. They established a relationship between mechanical and transmission properties of different linker groups, thereby providing valuable design rules for building molecular junctions.
4) Authors studied the transport properties for antiaromatic molecule juction, including Ni-norcorrole and Ni-porphrin. They demonstrate the higher conductance for antiaromatic molecule originated from LUMO orbital derived resonance being closer to the Fermi level when compared to its aromatic counterpart. And authors further showed that the antiaromatic electronic structure resembles a double p-doped aromatic molecule. And they provided the

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prediction how to tune the relative conductance of aromatic and antiaromatic compounds through the choice of linker.

Question:

(1) The DFT calculations for metal-molecular surface in this thesis are maostly performed by SIESTA code with a local-orbital pseudo-atomic basis. Have the authors checked the structural and electronic properties of you selected molecular/metal interface with other plane wave based DFT code, for instance, VASP or Quantum Espresso to confirm the chosen calculation parameters in SIESTA are appropriate?

(2) Surfaces can be approximated in DFT calculations through the creation of slab models. The slab should be thick enough such that there is no interaction between opposite surfaces through the bulk. The Chapter 2 and 3, carbene/Au(111) and donor-bridge-acceptor on Pt(111) interface, only three layers Au and Pt are considered, respectively. Is there any theoretical basis on that? Does the chosen specific Au or Pt layers have been tested?

(3) High spin states usually occur in TM-porphyrins molecular, which might depend on the interaction with the substrate. Do you think that such high spin state can be exist in your systems? Moreover, it is well known, that the electronic structures and spin states of metal-porphyrins may strongly depend on an employed DFT-XC method (PBE, hybrid, PBE+U). How does the electronic structures and spin states depend on the employed XC-functional for given systems?

In summary, the reviewed thesis is a high-quality scientific work that fulfills, in my opinion all requirement needed for obtaining a PhD degree. I therefore **recommend** the thesis of **Narendra Prabhakar Arasu** for the defense.

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