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**Report on the dissertation "Structural, electronic, and magnetic properties of nanomaterials for potential magnetic, energy storage, and catalytic applications" written by Rotislav Langer for obtaining the PhD degree at the Department of Physical Chemistry, UP Olomouc**

The dissertation summarizes the work of Mr. Langer on the theoretical study of the electronic and magnetic properties of molecular nanomaterials. This encompasses electronic structure calculations of different atoms on graphene, of porphyrin derivatives, and of graphene-based systems. In my opinion, the dissertation illustrates that the work carried out by the candidate is substantial and exemplifies the high quality of the research.

The thesis starts by presenting a historical introduction of materials science including the use of magnetic devices for data storage, up to the current state of the art of individual molecules. Chapter 1 lists the materials studied here, namely graphene and several derivatives, as well as metal porphyrins. Chapter 2 presents an overview of magnetism in these systems in the style of a review paper. The DFT-based theoretical methods used to compute the electronic structure are described in Chapter 3. Chapters 4 to 9 each summarize one publication from the candidate, which are reprinted as appendices.

The work is clearly structured and easy to follow. The methodologies are described appropriately and an overview of the importance of the questions addressed is given. The chapters dealing with the research papers properly summarize the main findings in them and their importance.

Concerning the body of the dissertation, it would have been useful to add a list of publications generated during the thesis. Apparently, the candidate produced 7 papers, although 3 others (presumable written elsewhere) are listed in Web of Science. Only 6 of them are, understandably, discussed in detail in the dissertation. However, to explicitly mention the list of publications would give a clear idea of the output generated during the thesis.

In my opinion, a more important drawback for the readability of the thesis comes from the abundance of acronyms, which makes it hard to follow some sentences. A list of abbreviations is presented at the beginning of the thesis but it is not sorted alphabetically, severely reducing its usefulness since it is not possible to search for the abbreviations which are not understood.

On the scientific side, I appreciate that the work addresses a topic at the forefront of current research. I also like the analysis of the results presented. I particularly value that the candidate has worked in close collaboration with experimental colleagues, which forces a repeated evaluation of the scope and purpose of the calculations. As such, this work has led to many publications. The dissertation and associated papers demonstrate that the candidate can perform and analyze quantum chemical calculations at a high level.

The output of the PhD work is quite impressive, as the candidate produced many publications, in good journals, and often in instances where calculations are complemented with experimental results.

At the same time, I have a few questions and suggestions, which will also serve as points of discussion during the oral examination.

- Chapter 4 investigates the structure, electronic and magnetic properties of P atoms on graphene. In the case of individual P dopants (eg. Fig. 30), one should calculate a single P atom on graphene, however this is not possible since (inevitable) periodic boundary conditions lead to this P atom being coupled to its replicas in the neighboring unit cells. What is the effect on the calculated electronic and magnetic properties of this limitation of the simulations? Results for two or three P substituent atoms (ie. on graphene vacancies) show that magnetic properties are determined by whether or not the P atoms lie on the same or different sublattices. From Fig. 30, the individual P dopant and its replicas would be on the same sublattice.

- In chapter 6, the dissertation discusses the magnetic anisotropy energy in porphyrin molecule and 1D chains. The main results are that the planarization induces a large modification in the magnetic anisotropy energy. Calculations show that this results from a rearrangement of pi orbital energies of the Fe d orbitals. Simulations are done both for freestanding systems as well as adsorbed on Au(111). Can you comment on how much of this effect comes from structural effects (distortion and planarization) and how much from charge transfer to/from the substrate? Is there any insight from experiments?

- Chapter 7 discusses the binding of Pt individual atoms on covalently-functionalized graphene. Identifying configurations where the Pt atoms do not agglomerate and have an accessible coordination sphere around them is important for single-atom catalysts. The main finding in this chapter is that only nitrile (-CN) groups form stable complexes with Pt adatoms exposed away from graphene while strongly anchored. The model considers two-sided functionalized graphene (adsorbates in the ortho or trans configuration). This is straightforward in the simulations, but in a real system (as shown in the accompanying experimental results), the graphene sheet is deposited on some substrate. Here, the functional groups facing the substrate would deform and corrugate the graphene sheet, or interact with it, deviating from the simpler picture provided by the simulations. Can you comment on this?

- Also about these results of chapter 7, simulations find that Pt atoms will break the bonds of the functional groups with graphene and replace them (except for -CN). A measure of the ability of Pt to do this comes from the strength of the binding of the different species with graphene. Table 4 shows the calculated binding energies of the different adsorbates. This is highest for Pt for 1 adsorbate, and very high compared to the others for 2 adsorbates, establishing the strong binding of Pt atoms to the graphene sheet. Why does Pt displace a F atom for example (with comparable or even stronger binding than Pt) but not CN groups? What are the driving forces that one should consider to understand the formation of these complexes?

In summary, I find this doctoral work to be of very good quality. The level of the calculations is high, the scope of the problems addressed is ambitious and timely. In his PhD, the candidate has cooperated closely with experiment. The work had resulted in many publications at a high level.

I believe that, altogether, this establishes that Mr. Langer can carry out independent research, as also evidenced by the number of papers where he is first author. I look forward to discussing these topics with the candidate in the oral examination.

Sincerely,

**Héctor Vázquez**
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