

Opponent: Ing. Dominik Legut, Ph.D.

Author of the Ph.D. thesis: Ing. Barbory Hanulíková

Supervisor: doc. Ing. et Ing. Ivo Kuřitka Ph.D et Ph.D

Title of the Ph.D. thesis: **Electronic properties of polysilylenes studied in silico on oligomers in various conformations**

Main objective of the work is a study of the electronic properties and hence derived physical properties like optical transitions at UV-VIS, Raman and IR energy range on polysilylenes with conformation changes, i.e. a kink. The thesis is composed of the brief overview of methodology, aims of the work, summary of the main results and attached five papers. Three papers were already published and two were submitted. To my concern, this style is very much suitable and number of papers is appropriate and therefore I evaluate it as very positive result.

The thesis itself is very well structured, however too brief. Also, its content often does not highlight the most important results derived from the quantum chemistry calculations reported within the articles. For instance from article I and II I would emphasize the UV-VIS spectra being the major results (from figs taken from tables 2 and 3, article I). Also to add more details about calculations of the UV-VIS spectra into the theory chapter would be very beneficial. The justification of the different exchange-correlations (B3LYP, M06 and wB97X-D) and their empirical parameters used in article III needs also more details in the theory. Here is a list of general and formal remarks and comments:

General:

- Generalized gradient approximations is “non-local”, it takes local value and the gradient. All exchange-correlations approximations except LDA and LSDA are non-local.
- No explanation in theory about the “PM3 level”, a methodology for the results reported in article I?
- No explanations about B3LYP a 6-311G, eventually 6-31G\*, p. 11, 13? Of course I know...but not a general reader.
- Why the HF approach is explained if none of the results are calculated with it? All results are calculated with DFT or time-dependent DFT about which is not a single note written?
- In section 6.2. is not obvious, which results are obtained using DFT or TDFT?
- So-called red shift is anticipated result concerning the width of the band gap as function of the Si length for both OMPSi and ODMSi, and which comes to the constant value.
- From fig. 8B is visible that the most stable configuration has dihedral angle rather closer to the 155 than between 160-165 degree?
- In fig. 8B relative energy is relative to what? I would expect here to relative to case 10 (without kink). The figure would be then more readable. More important is, what is the meaning that the case 10 (black symbols) have for some angle the least negative energy, i.e. the least stable configurations? What kind of energy is presented in fig. 8A?
- I do not think it is possible to make energy differences among calculations using different exchange-correlations approximations. Actually DFT is for using differences of the energy, not the absolute values. What is the exact difference among B3LYP, M06 and wB97X-D? This is missing in theory part. In fig. 10 it would be beneficial to show which variant 10-X has the lowest energy?
- What is the extension of polaron?
- Electron-phonon interaction is much complicated than the formula displayed (eq. 6) and more over the formula is not mention at all in Ref. 12, which is here cited.



Formal:

- missing Ref. 51, indeed refs. 52 a 53 are before 51
- not grouped references, e.g. [1-4] instead of [1,2,3,4]
- typos, e.g. p. 14 allows → allow
- figures are in poor quality and inadequate font choice in figures
- figure 12 is not well scaled

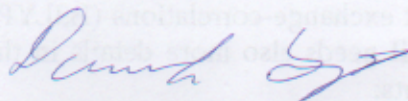
Comment:

- error of 0.1-0.5eV in spectra rigid shift is not much, but if the error is given to some precisely defined quantity, e.g. to the HOMO, then 0.5eV is a large error

Summary:

The thesis is well written in English and it is its benefit not to write it in czech for a large dissemination potential for worldwide community. However, the thesis itself is too brief and simplified to my humble opinion, i.e. actually without proper theory derivations. With all the above remarks and comments taken into account I recommend it for the defense.

In Ostrava, June 21<sup>st</sup> 2016



Ing. Dominik Legut, Ph.D.  
IT4Innovations Center,  
VSB-Technical university Ostrava  
708 33 Ostrava-Poruba