Referee's report on PhD thesis

Tereza Vitvarová

Synthesis and Properties of Supramolecular Polymers

The presented thesis deals with the synthesis of a new type unimers usable for construction of metallo-supramolecular polymers (MSP) and description of the properties of the unimers as well as of the MSP. Five new unimers containing a phosphole central unit and two terpyridine end-groups connected by different conjugated linkers were prepared by multistep syntheses. MSP were prepared with several metal cations (Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) and their properties determined using spectroscopic techniques and size exclusion chromatography (SEC).

The thesis is written in the English language, clearly, following the standard structure, and besides the text itself (105 pages) also contains as attachments full texts of the published papers which came up from work. The theoretical part of the thesis describes sufficiently the present status in the area MSP and phosphole chemistry, citing over 100 relevant publications. The Results part is divided into sections describing synthesis and characterization of monoterpyridine ligands, unimers, and MSP (1:1 unimer/metal cation). The last sections of Results are dealing with studies of the properties of MSP, depending on the cation/unimer ratio. UV/vis absorption and fluorescence spectra of solutions, as well as thin films, are described and reasonably discussed in detail as well se SEC of kinetically stable MSP. In the Experimental part are well described all procedures used in the experiments and all new compounds very well characterized (^{1}H, ^{13}C NMR, ^{31}P NMR, IR, HRMS).

Nevertheless, I have some comments and recommendations for the author:

- On page 25, the analysis performed by HypSpec software is named "factorial analysis". The correct name is "factor analysis".
- There is only a small number of typos and grammatical errors in the text; but several times, a temperature was given without a space between the number and the unit (pages 36, 79, 84).
- On page 45, retrosynthetic arrows are drawn in the wrong direction (they should point from the product to starting compounds).

There are also some questions for discussion:

- What is the mechanism of the phosphole formation reaction depicted in Scheme 11?
- The boronate shown in Scheme 16 is described as unstable. What is the decomposition product?
- What was the thickness of thin films of MSP from which their spectral properties were obtained?
- What is the principle of the method used to determine the quantum yield of fluorescence?
- How would you explain that only Zn^{2+} based MSP exhibited fluorescence and no fluorescence was observed for MSP base on the other tested metal cations?
- Was a half-life of the prepared kinetically stable MSP determined? What is its typical value?

Despite the above critical comments I consider the thesis to be well written and the results are interesting. Its quality was also confirmed by two papers related directly to this work (published in impacted journals) in which Tereza Vitvarová is the first author. Therefore, I recommend the thesis for defense.

Prague, April 20, 2017

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