Review of the thesis submitted by Ms. Tereza Vitvarová

Ms. Tereza Vitvarová submits her thesis entitled "Synthesis and Properties of Supramolecular Polymers". This work was realized under the supervision of Prof. Jiří Vohlídal (Charles University in Prague, Czech Republic) and Prof. Muriel Hissler (Université de Rennes 1, France). The document (~100 pages + annexes) is divided in several three main Chapters and Annexes.

The first Part is an interesting general introduction as well as a bibliographical section that reports the main concepts of Metallo-Supramolecular Polymers. The synthetic strategies and the main properties of these particular polymers and their subunits (chelating ligand, spacers…) are described. The particular properties of the phosphole unit and examples of phosphole-containing organic polymers are also reported.

The second main part reports the experimental data and results obtained by Ms. Tereza Vitvarová. The global objective was to prepare and investigate new conjugated metallo-polymers in which the organic part associates terpyridine as chelating ligand with phosphole and thiophene units as spacer. A large part of this work was dedicated to the synthesis of the organic ligands. This type of association is very uncommon and promising. It is clear that the preparation of such systems requires a great experience in organic and organometallic synthesis and in particular in the chemistry of the Phosphorus element. Several original compounds (unimers) have been successfully prepared and characterized in particular by spectroscopy (NMR, absorption and emission spectroscopies essentially). In addition, an interesting C-H activation of phosphole species has been achieved.

The reactivity of these organic compounds with transition metal cations (Zn$^{2+}$, Fe$^{2+}$, Ni$^{2+}$, Cu$^{2+}$) was then investigated. The formation of the metallo-supramolecular polymers was unambiguously
demonstrated. Their properties and their formation were investigated using mainly spectroscopy as well as size exclusion chromatography (SCE). Importantly, it was shown that the introduction of the phosphole unit between thiophene groups increases the extent of delocalization in the unimer molecules. This result confirms the great interest of the phosphole group. In addition, some important differences (e.g. fluorescence properties and stability) were observed in particular between \( \text{Zn}^{2+} \) and \( \text{Fe}^{2+} \) systems.

The end of this manuscript includes also a well-written experimental part, a short conclusion, references and annexes.

In conclusion, this thesis reports very interesting results in the field of metallo-supramolecular structures incorporating phosphole units. The work done in the thesis is exhaustive and two international publications have been already reported. For these reasons, it is clear that this thesis of Ms. Tereza Vitvarová is recommended for the award of the degree.

Professor Guy ROYAL
Université Grenoble Alpes