

**POSUDEK RECENZENTA DOKTORSKÉ DISERTAČNÍ PRÁCE  
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**NOVEL CONJUGATED POLYMERS OF THE METALLO-  
SUPRAMOLECULAR AND POLYELECTROLYTE CLASS**

The PhD Thesis of Mgr. Sviatoslav Hladysh is concerned with the synthesis and characterization of two groups of conjugated polymers: One product group were metallo-supramolecular polymers (MSPs) composed of conjugated heteroaromatic oligomeric building blocks called unimers, which were linked via coordination bonds to longer chains by cations of several transition and lanthanoid metals. The unimers were electro-neutral, so that the main chains of the prepared MSPs were positively charged and accompanied by anions. The second group of synthesized products were water-soluble polythiophene polyelectrolytes containing ionic pendant groups, namely hexyl chains terminated by phosphonium ions, which were of interest as such (e.g. for fluorescing sensor applications), or as precursors to unimers well-soluble in water.

The topic and context of the PhD Thesis is very attractive: Dynamers are a novel group of materials which – due to the reversible formation of their backbone – offer unusual processing possibilities: Their viscosity is tuneable in a very wide range via thermodynamic control of chain length (e.g. by coordinating solvent and/or temperature change). Additionally the studied MSPs display self-healing properties, a potentially interesting redox chemistry, as well as attractive electro-optical properties. The water-soluble polythiophene derivatives, on their part, offer the possibility of processing the organic semiconductor polythiophene from such environmentally friendly solvents like water. Both product groups are of interest for applications in the field of electronics, electro-optics (OLED, FET-transistors, photovoltaics), or sensors.

In the first part of his work Mgr. Hladysh prepared numerous unimers and ligands (all containing tridentate functional units) starting from the cheap chelidamic acid. One group of such products was based on the 2,6-bis(benzimidazol-2-yl)pyridin-4-yl unit, namely the monotopic ligands “*bzimpy-OH*” and “*bzimpy-T*” (model compounds), as well as the unimer “*bis-bzimpy-T*”. As a part of these syntheses also the easily deprotonable unimer “*bis-dopy-T*” with pyridine-2,6-dicarboxylic acid end groups was also prepared. Another group of synthesized ligands and unimers was based on 2,6-bis(oxazolyl)pyridine, namely the monotopic ligands “*pybox*”, “*pybox-Th*” and the unimers “*P-Th*”, “*P-Bt*” and “*P-Te*”, which were characterized by improved solubility. The *bzimpy*-based ligands and unimers were tested in complexes and MSP compound with  $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$  cations, while the better-soluble *pybox* derivatives were combined with  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  cations. The resulting *pybox*-based MSP solutions were well-suited for spin casting of MSP films. These novel products combined seldom used conjugated chelate groups with oligothiophene-based short

chains (thiophene-2,5-diyl, bithiophene-2,5'-diyl, thienothiophene-2,5-diyl and terthiophene-2,5''-diyl units have been used), which were connected to fully conjugated larger units. Differences in relaxation possibilities or in the ability of metal-ligand charge transfer, or metal interactions with the pi system of unimers led to interesting electrooptical properties. Generally, only the  $\text{Zn}^{2+}$  cations were found to support fluorescence of the MSP molecules, while the other ones quenched it. Solid-state UV/Vis absorption and fluorescence were extensively studied, and the stacking behaviour of different unimers and MSPs was clarified by X-ray diffraction analyses. Studies of MSP dynamics via UV/vis and NMR-spectroscopy indicated an easy formation of butterfly complexes with two tridentate ligands, as well as the dynamer chain degradation with excess cations.

The water-soluble polythiophene derivatives, which were studied in the second part of this work, were obtained via preparation of bromohexyl-substituted dibromothiophenes and their subsequent Grignard metathesis polymerization. The synthesis was optimized to achieve relatively high molecular masses ( $M_n$  up to 9 000 g/mol  $\equiv$  cca. 37 repeat units) and very high head to tail regio-regularities (up to 94%). Quaternary phosphonium cationic groups were generated at the ends of the bromohexyl side chains via reaction with triethylphosphine or triphenylphosphine, where the first reaction occurred nearly quantitatively, while the other only to cca. 50% conversion. High water solubility was achieved in both cases, and optical absorption, as well as electro-luminescence was studied in DMSO, methanol and water. Aggregation in water was proven, as well as efficient fluorescence quenching with potassium ferricyanide and ferrocyanide.

**To sum up**, during his PhD studies, Mgr. Hladysh carried out a considerable amount of synthesis work, complemented by systematic product characterization, especially of electrooptical properties and of chemical structure, but also of molecular assembly dynamics, of molecular weights and of crystallization behaviour of some products. The results were published in four scientific papers which appeared in well-respected journals (2 papers as first and corresponding author, 2 more as important co-author). The synthesized products are very attractive and the synthesis concepts inspiring. The Thesis is well-written, typographic errors or stylistic imperfections are rare. Also the Introduction chapter is comprehensive, well-researched and attractively presented. The Figures and Schemes throughout the entire Thesis are of good quality. The Conclusions are logical and well-supported by experimental evidence.

**Recommendation**

The submitted PhD Thesis hence clearly shows, that Mgr. Sviatoslav Hladysh can work as a self-reliant and efficient researcher, that he can resolve demanding scientific tasks, and that he also successfully presents his results. Hence I clearly recommend the PhD Thesis of Mgr. Sviatoslav Hladysh for defence, and as the basis for granting him the scientific title PhD.

## Comments / Questions

- Comment to Introduction page 11, line 3 from bottom: Hydrogen bridges are more than just dipole-dipole interactions, typically they come close to coordination bonding with H as acceptor; true bonding is achieved in H-bridges in boranes (3-center-2-electron bonds) or in the bifluoride anion ( $\text{HF}_2^-$ ). The donor atom has to be a hard Lewis base: For example, there is no hydrogen bonding in anhydrous liquid HCl, in spite of the molecules' polarity.

- The Grignard metathesis polymerization is an interesting route. It would have deserved a more detailed reaction scheme, and also a scheme explaining the action of the  $\text{Ni}(\text{dppp})\text{Cl}_2$  catalyst (either in the Introduction or in the Results and Discussion).

- The content of the publications in Appendices C and D is only modestly presented in the Results and Discussion chapter.

1) Question: What would be the estimated fluorescence quantum yield of the water soluble polythiophenes in aqueous solution?

2) Question: What was the origin of the color change of the P-Th/ $\text{Fe}^{2+}$  complex after 1 month, as depicted in Appendix A?

3) Question of academic curiosity: Among the tested metals, V (e.g. as  $\text{VO}^{2+}$ ), Cr or Mn were avoided. Are these cations problematic? According to literature, Cr should form fairly stable complexes with terpyridine. Would it be possible to replace Zn with Mg?

4) Question of academic curiosity: The ligands *bzimpy* or *dopy* could be partly or fully deprotonated. Would there be a possibility to prepare neutral MSPs with such deprotonated unimers, e.g. using  $\text{V}^{4+}$  ?

5) Question of academic curiosity: Would it be possible to terminate the GRIMP polymerization by addition of bromine, in order to obtain Br-terminated polymers?